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Jung

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(54) **METHODS OF MANUFACTURING
ABRASIVE PARTICLE AND POLISHING
SLURRY**

(58) **Field of Classification Search**
USPC 252/79.2, 79.1; 438/692, 693; 451/41
See application file for complete search history.

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(56) **References Cited**

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U.S. PATENT DOCUMENTS

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(KR)

2011/0045745 A1* 2/2011 De Messemaeker et al. ... 451/41

(*) Notice: Subject to any disclaimer, the term of this
patent is extended or adjusted under 35
U.S.C. 154(b) by 0 days.

FOREIGN PATENT DOCUMENTS

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CN	1366549 A	8/2002
JP	8325558	12/1996
JP	2001047358 A	2/2001
JP	2008515764 A	5/2008
JP	2012104800	5/2012
JP	2013016830 A	1/2013
JP	2013104023 A	5/2013
JP	2013111725 A	6/2013
JP	2013119131 A	6/2013
KR	200596014 A	10/2005
KR	201174532 A	6/2011
TW	201137065 A	11/2011

* cited by examiner

(30) **Foreign Application Priority Data**

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Primary Examiner — Roberts Culbert

(51) **Int. Cl.**

C09K 13/00 (2006.01)

C09G 1/02 (2006.01)

C09K 3/14 (2006.01)

C01F 17/00 (2006.01)

(57) **ABSTRACT**

Provided is a method of manufacturing an abrasive particle including a mother particle and a plurality of auxiliary particles formed on a surface of the mother particle, and a method of manufacturing a polishing slurry in which the abrasive particle is mixed with a polishing accelerating agent and a pH adjusting agent.

(52) **U.S. Cl.**

CPC **C09G 1/02** (2013.01); **C01F 17/0043**
(2013.01); **C09K 3/1409** (2013.01); **C09K**
3/1445 (2013.01); **C09K 3/1463** (2013.01);
C01P 2004/40 (2013.01)

19 Claims, 19 Drawing Sheets

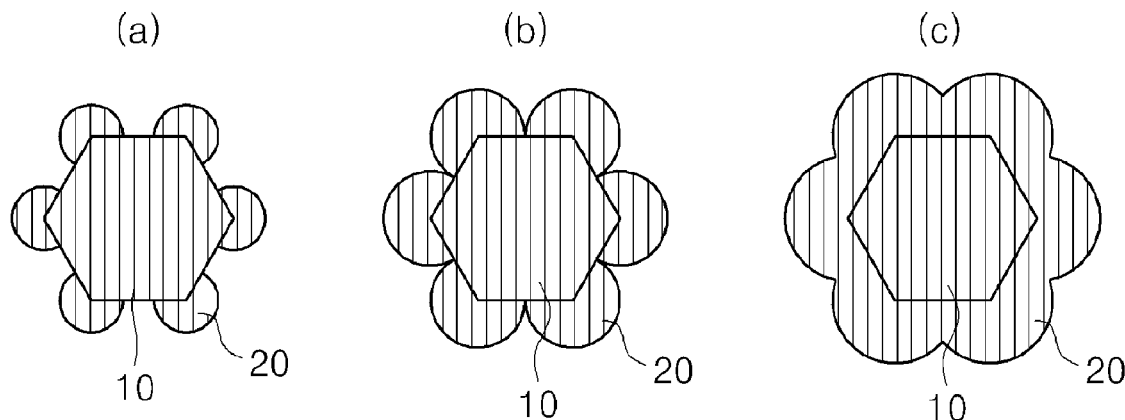
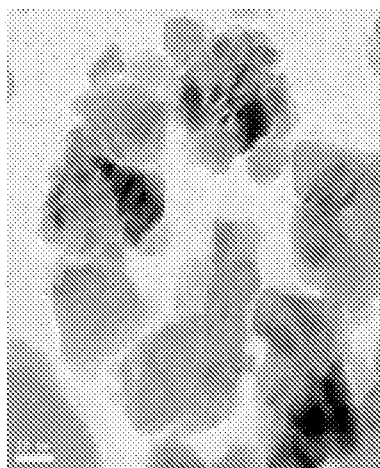


FIG. 1

(a)



(b)

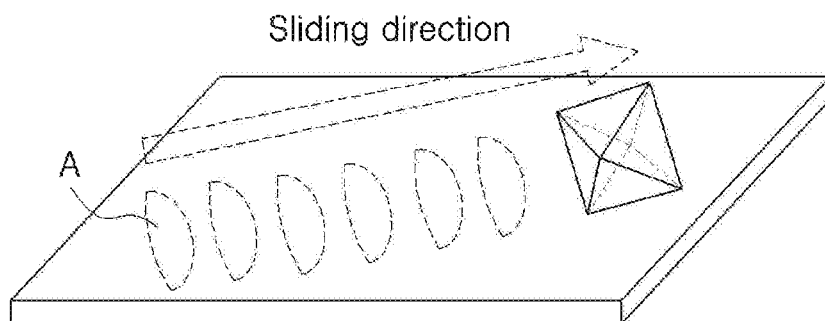


FIG. 2

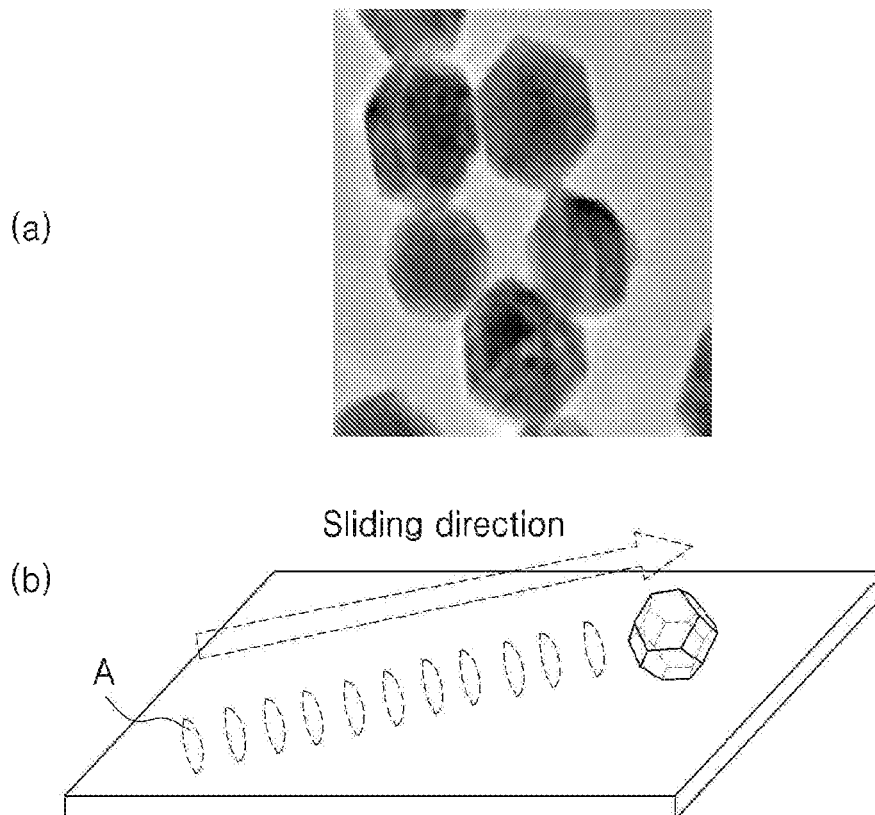


FIG. 3

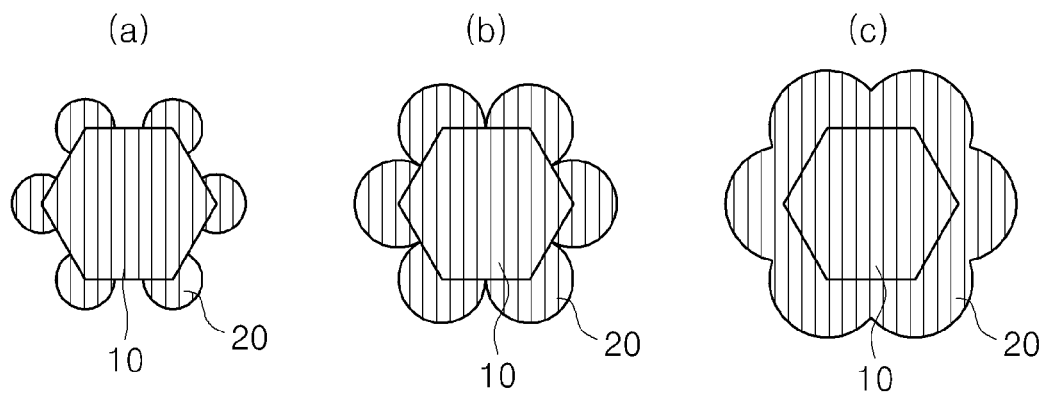


FIG. 4

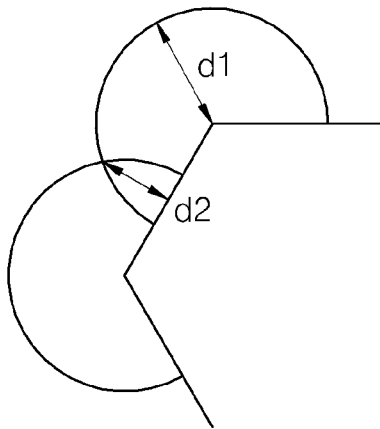


FIG. 5

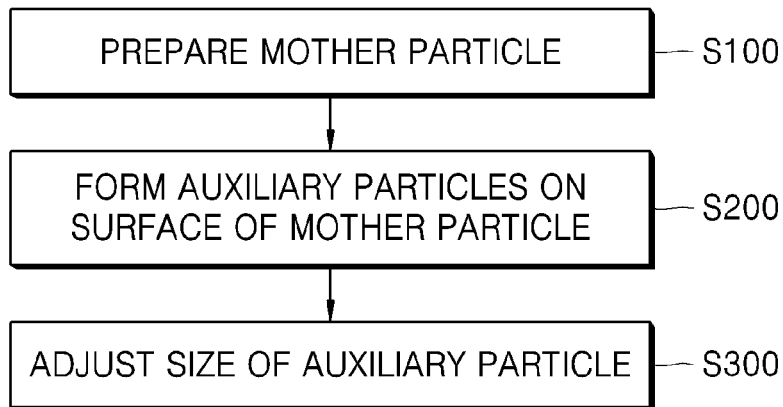


FIG. 6

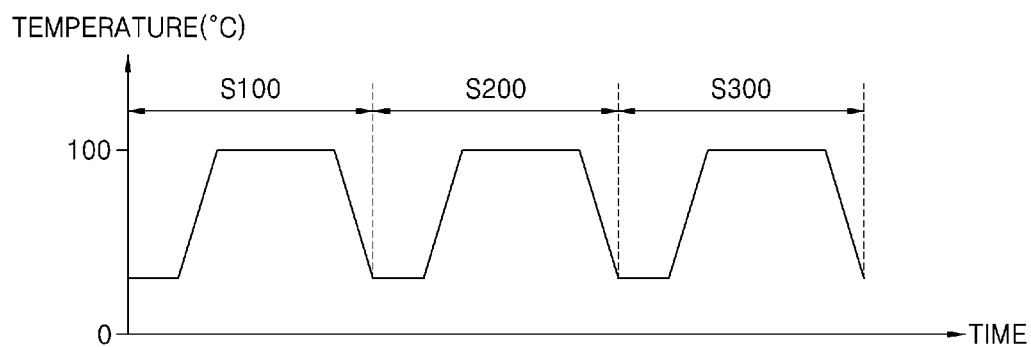
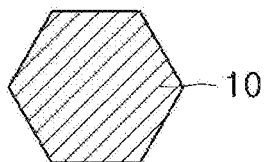


FIG. 7

(a)



(b)

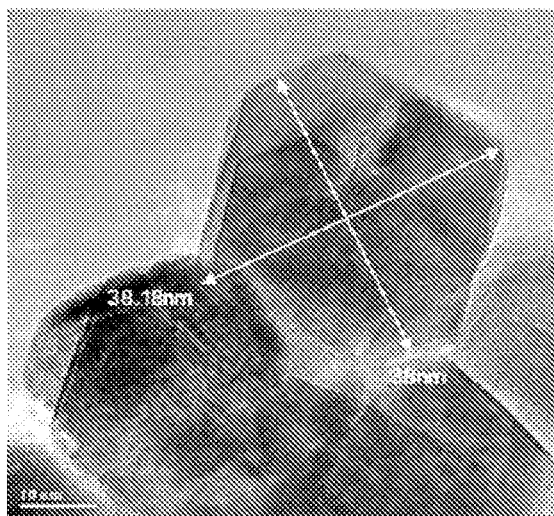
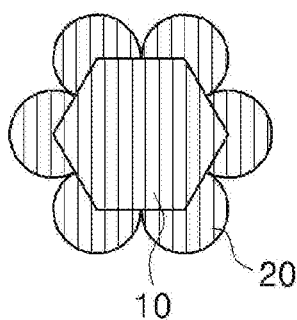


FIG. 8

(a)



(b)

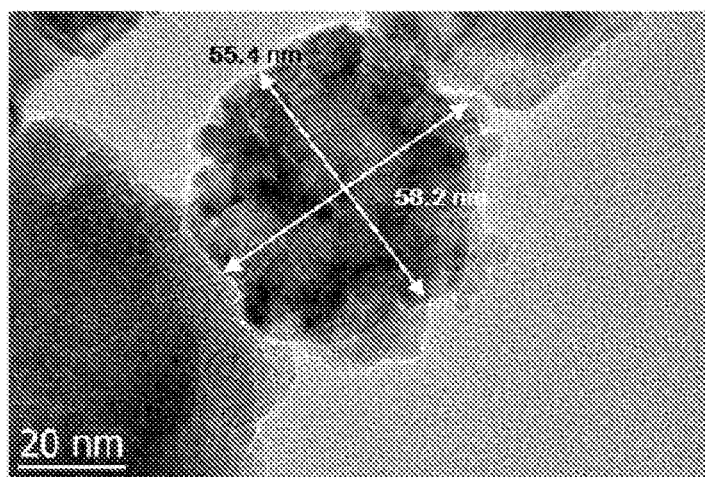


FIG. 9

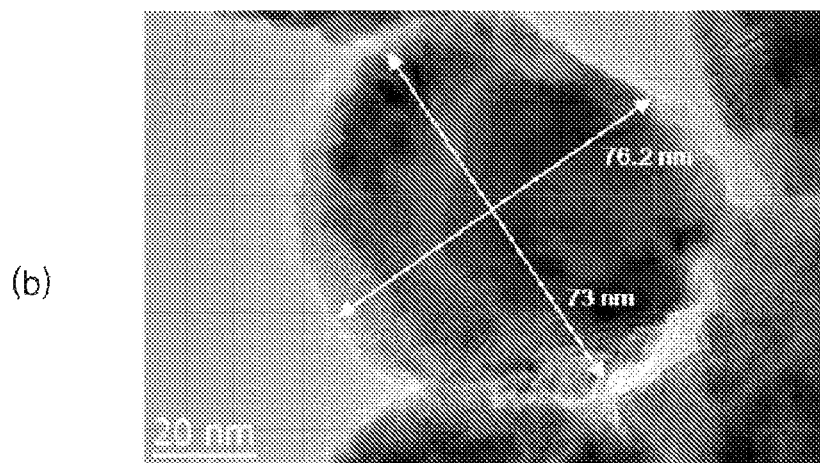
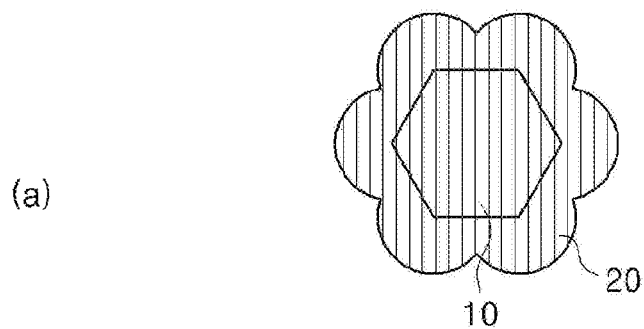


FIG. 10

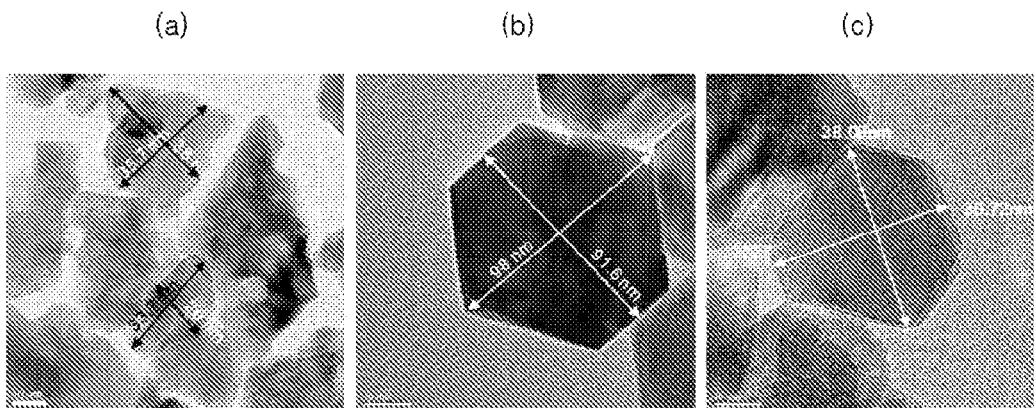


FIG. 11

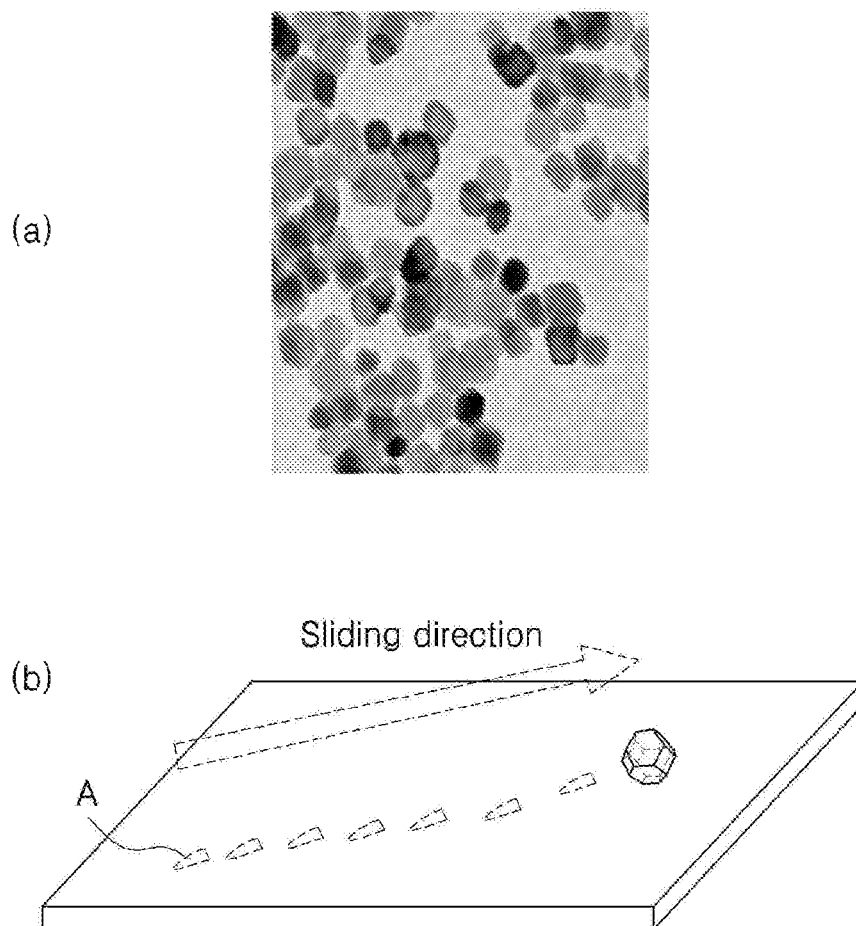


FIG. 12

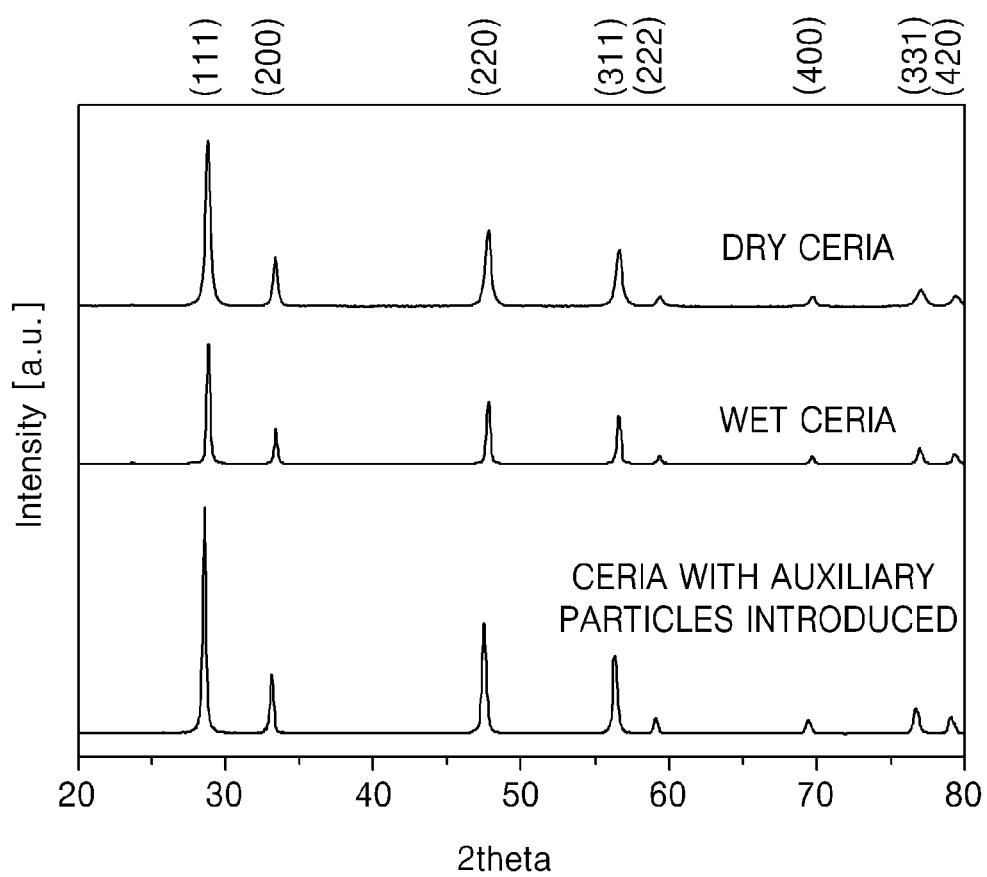


FIG. 13

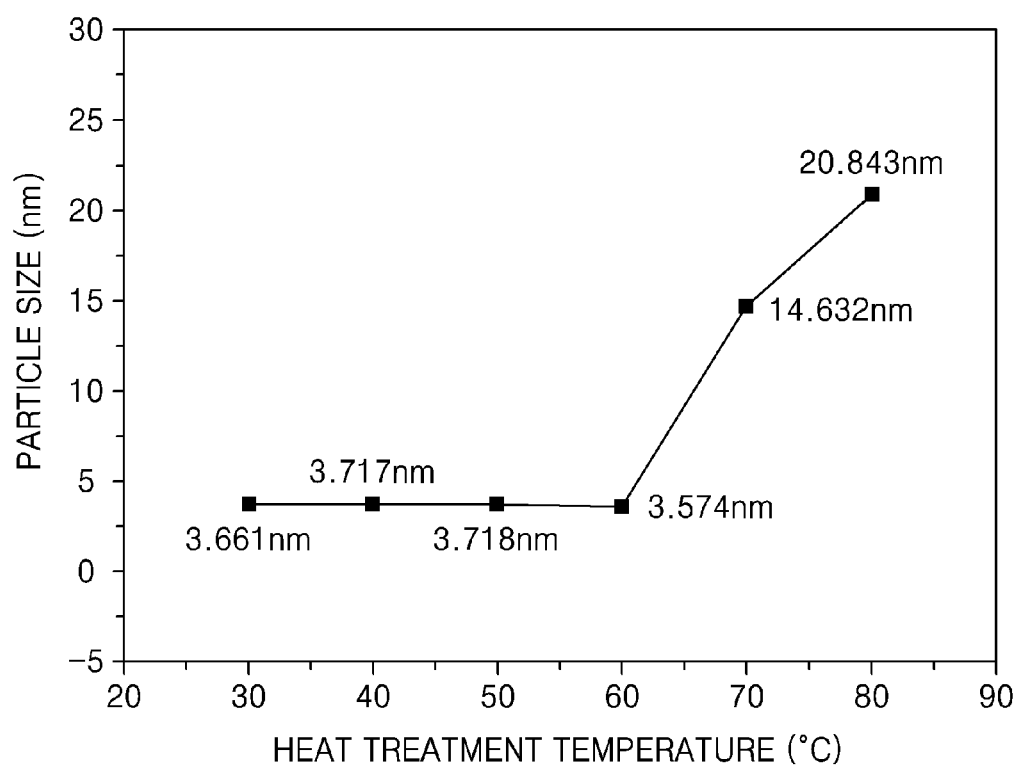


FIG. 14

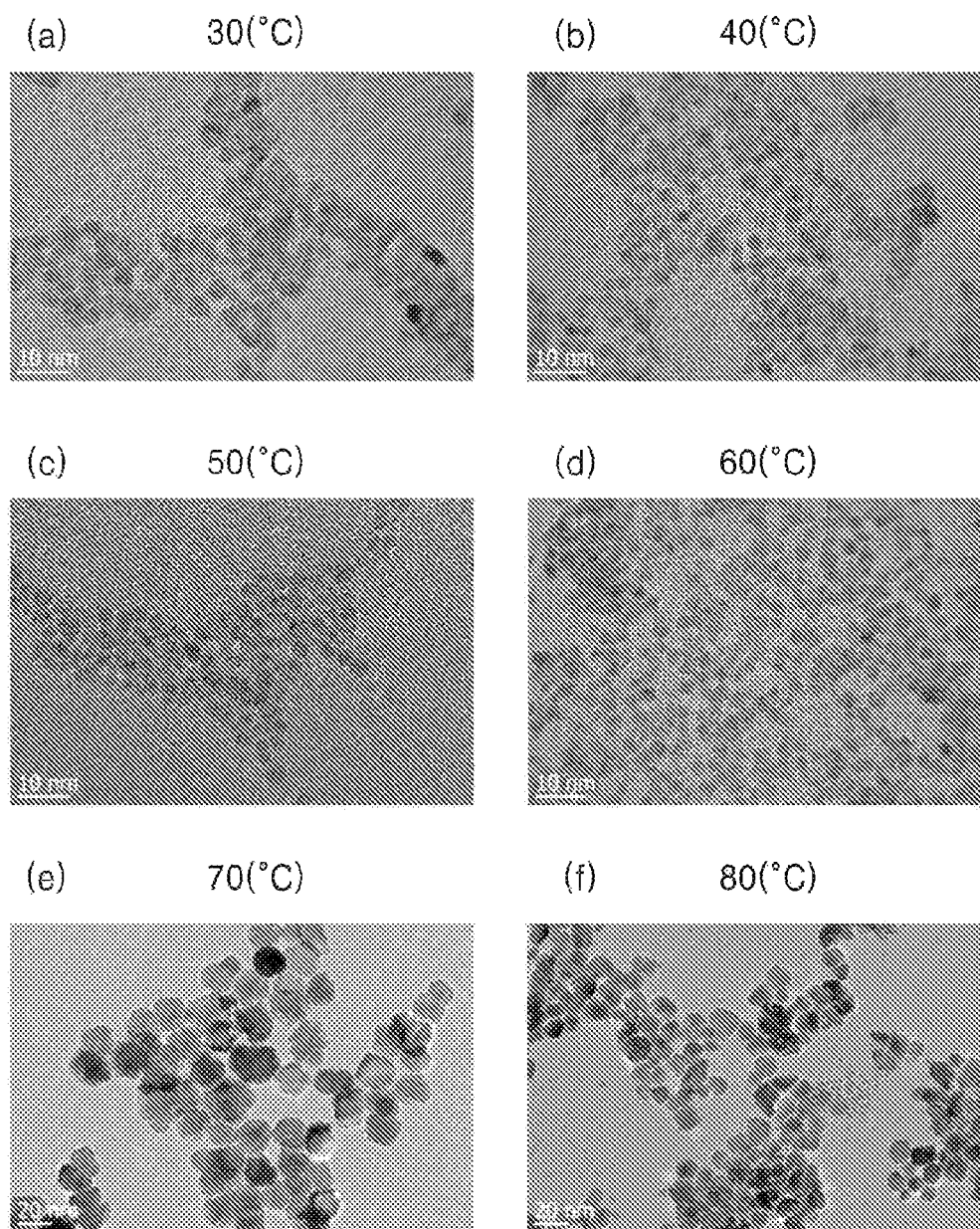
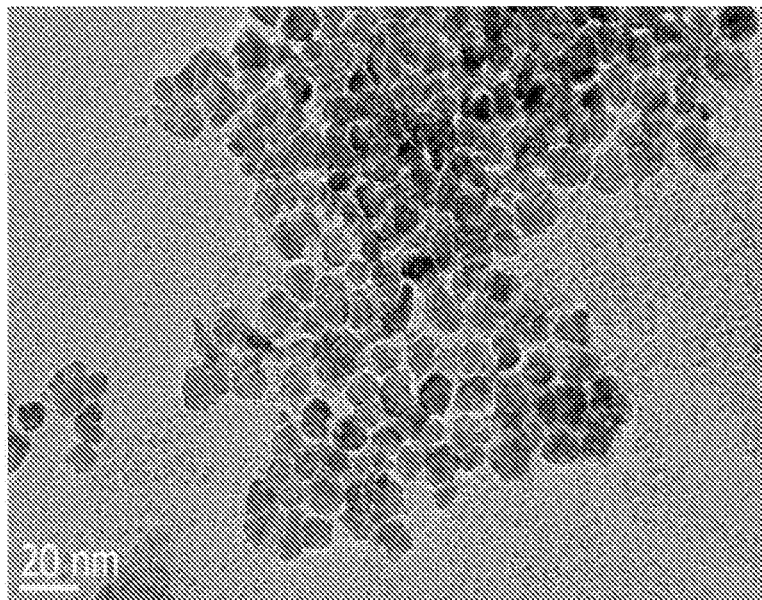


FIG. 15

(a)



(b)

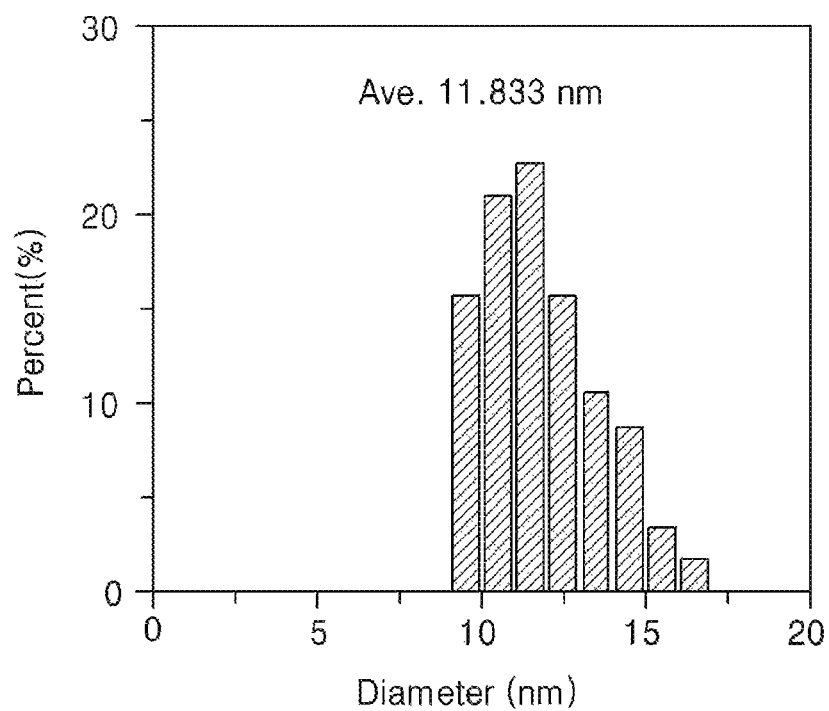


FIG. 16

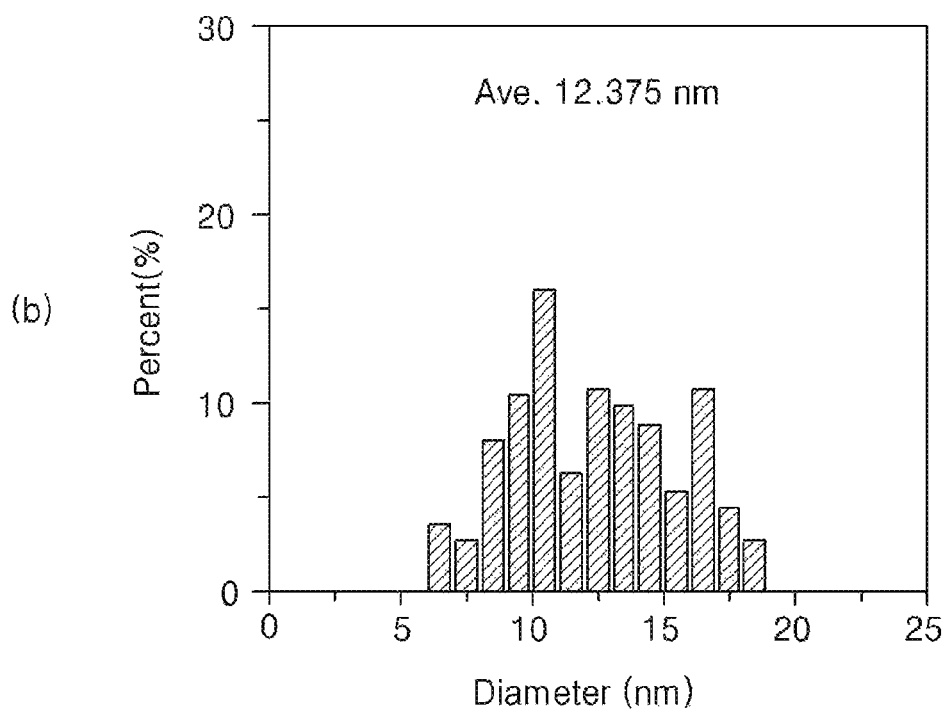
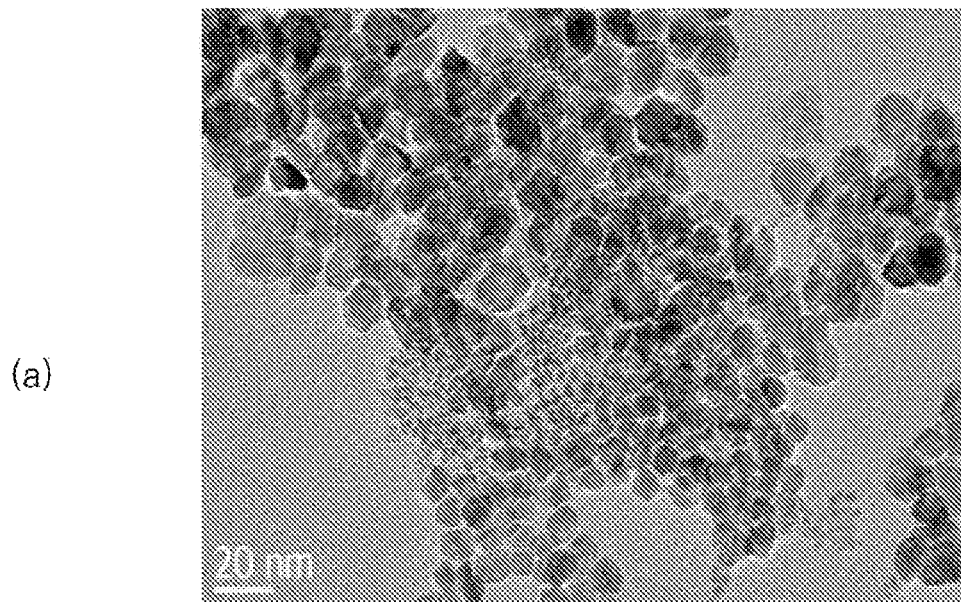


FIG. 17

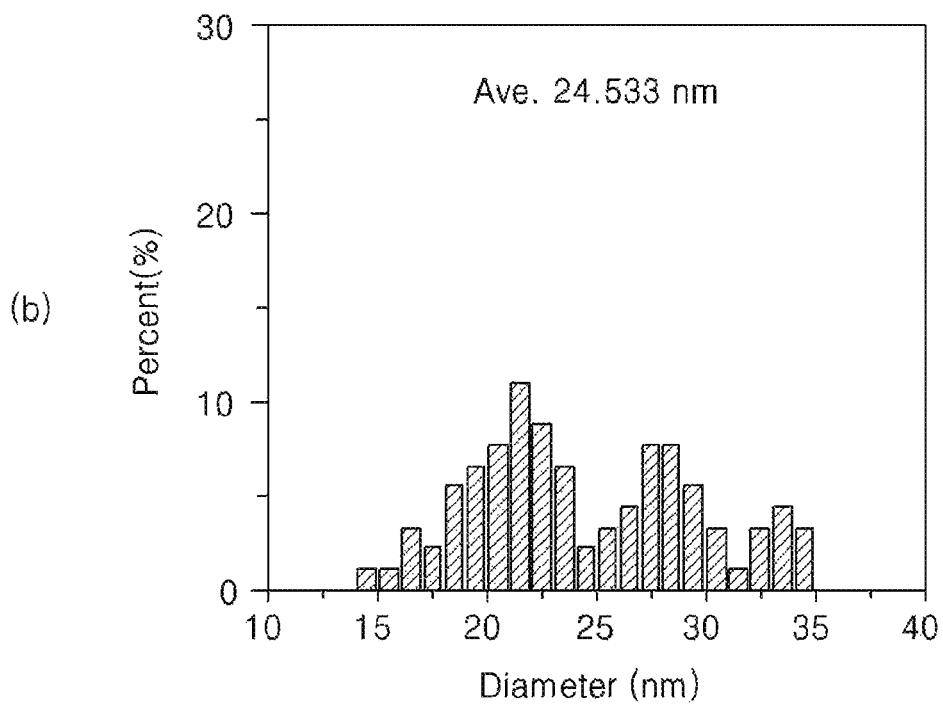
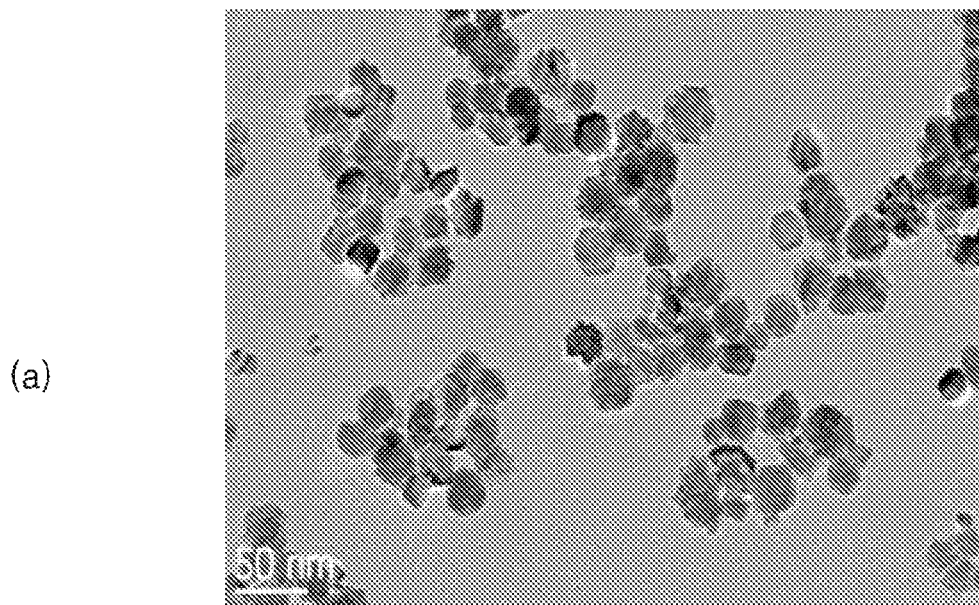


FIG. 18

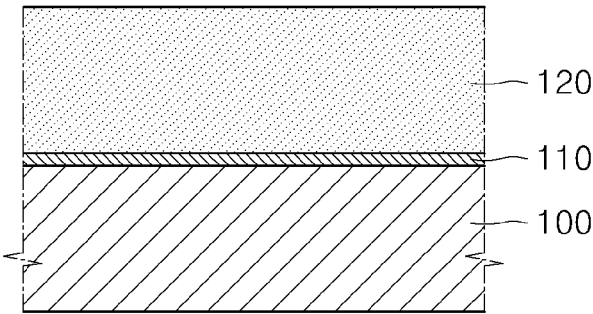


FIG. 19

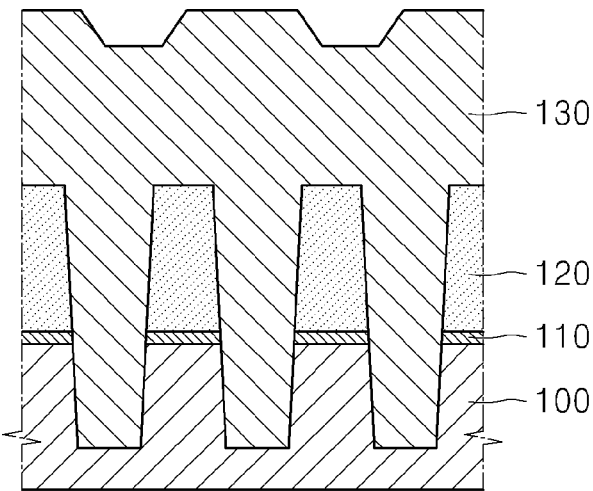


FIG. 20

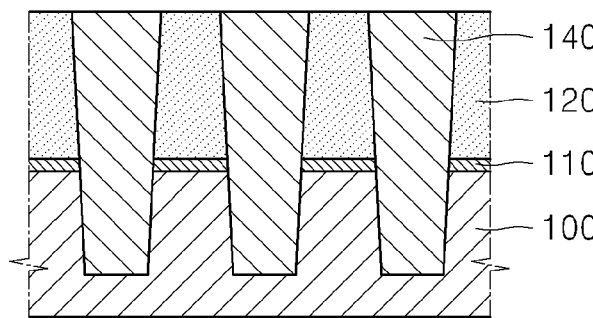


FIG. 21

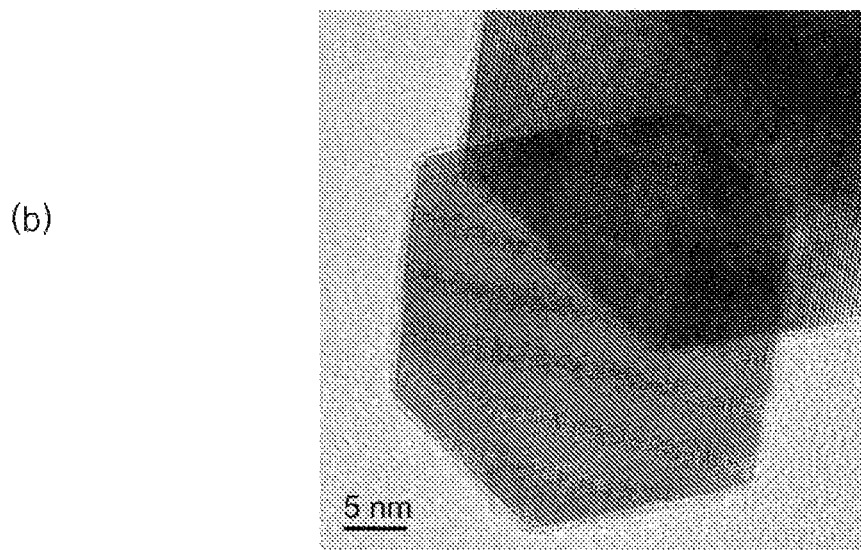
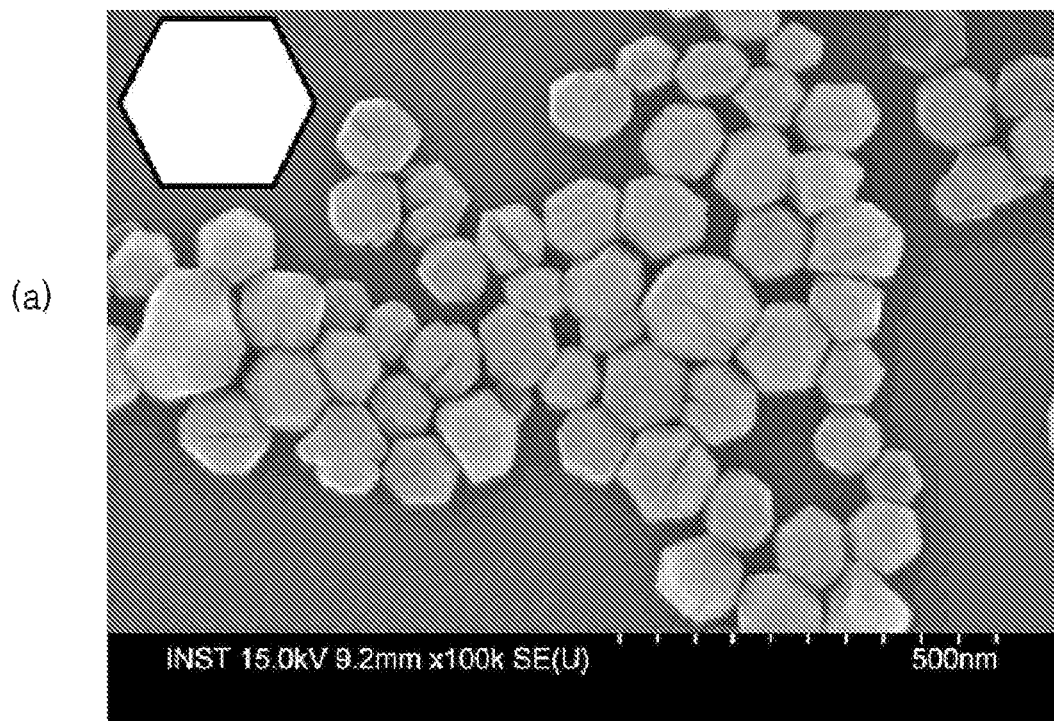


FIG. 22

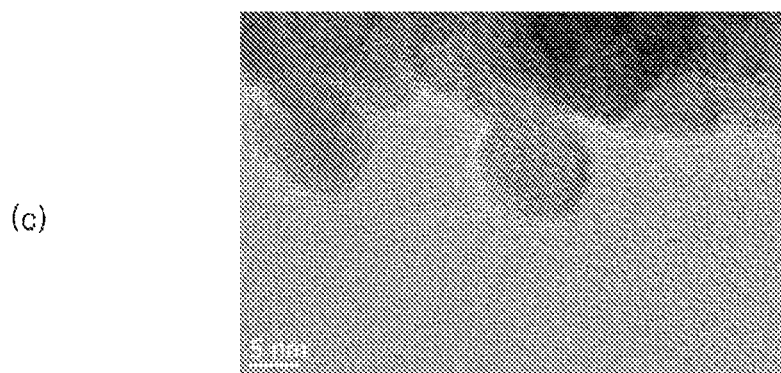
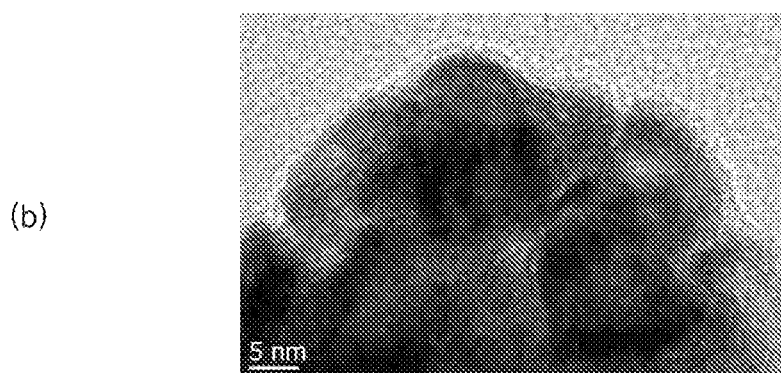
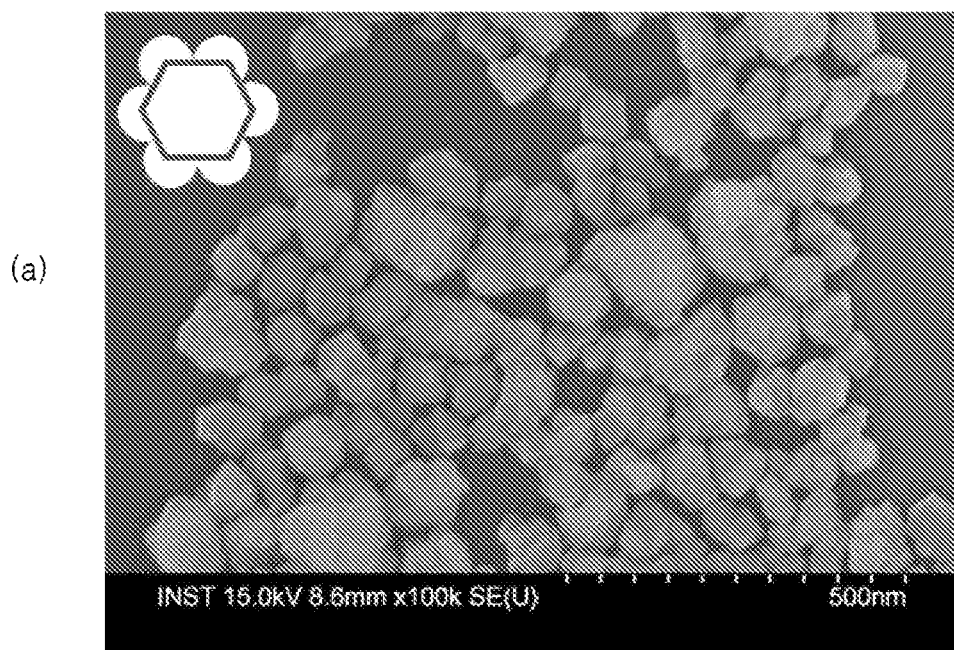


FIG. 23

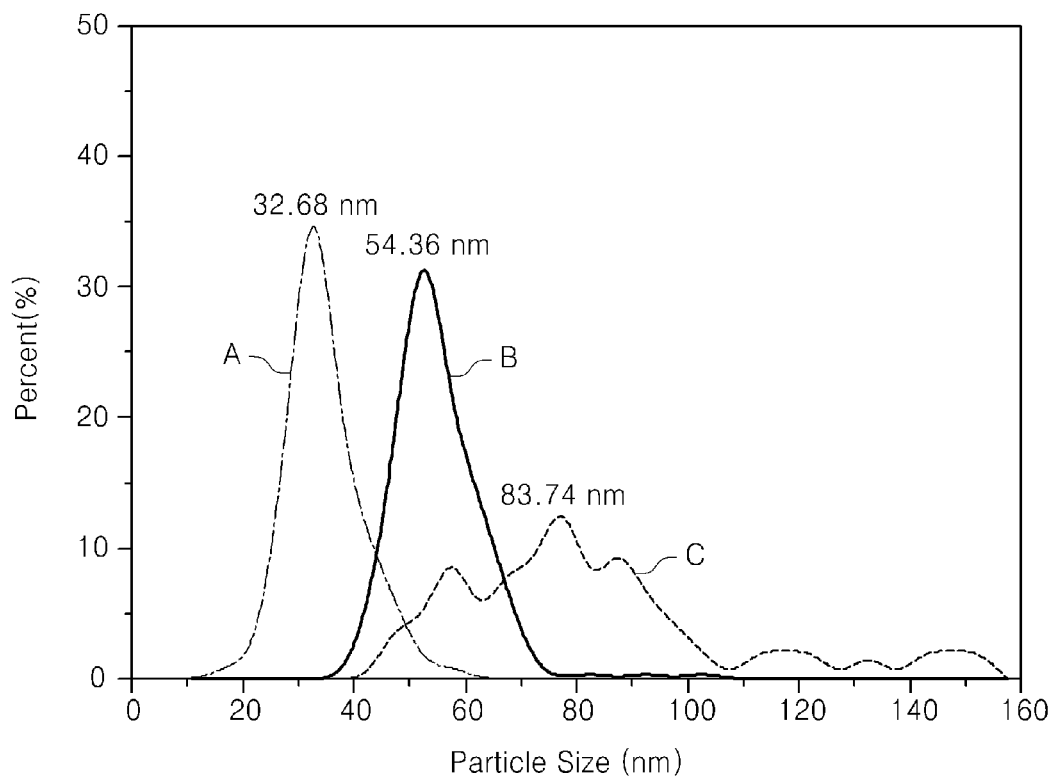


FIG. 24

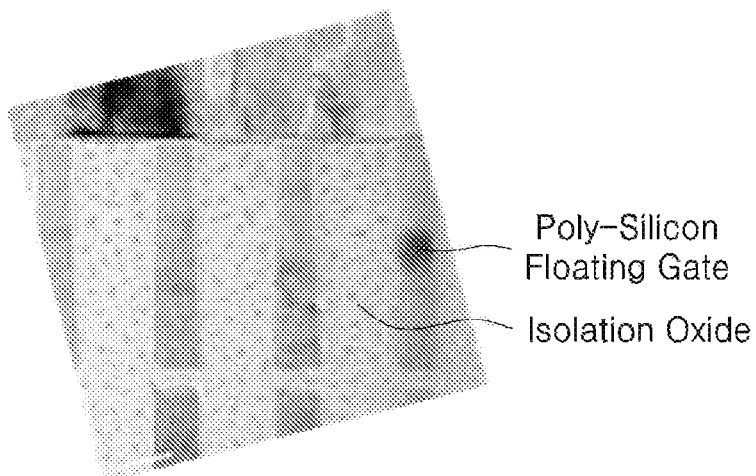


FIG. 25

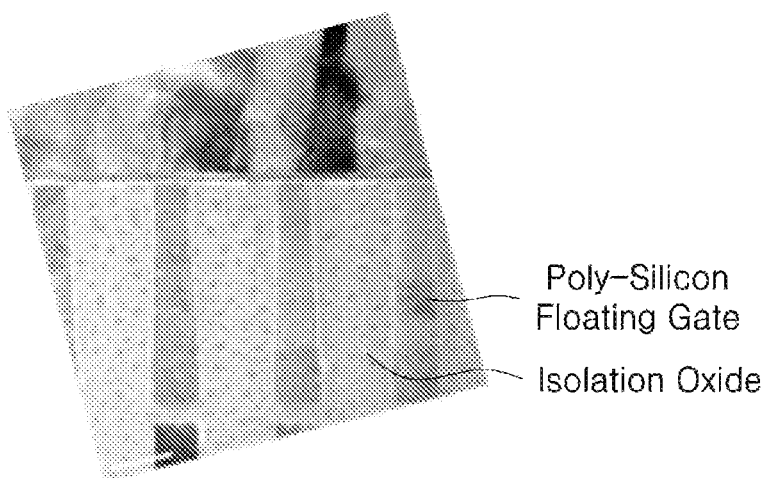


FIG. 26

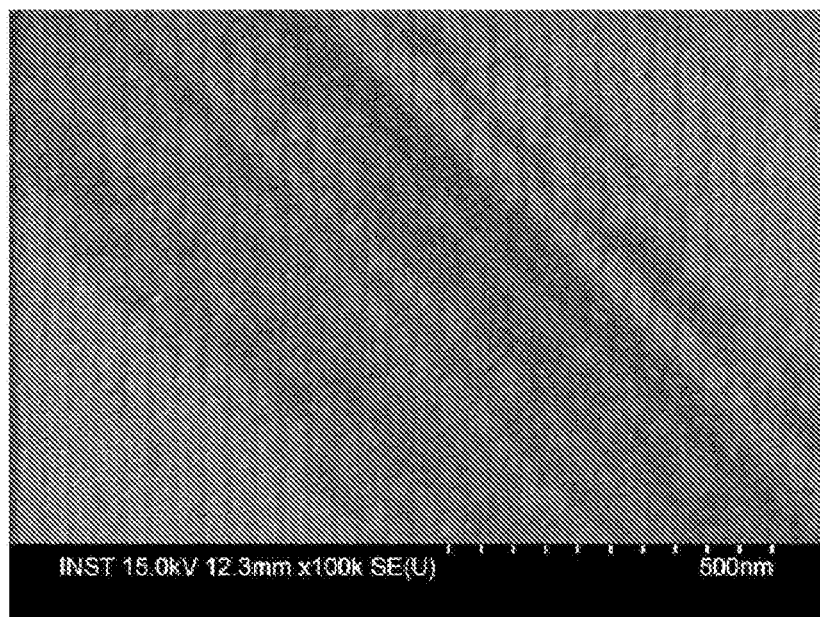
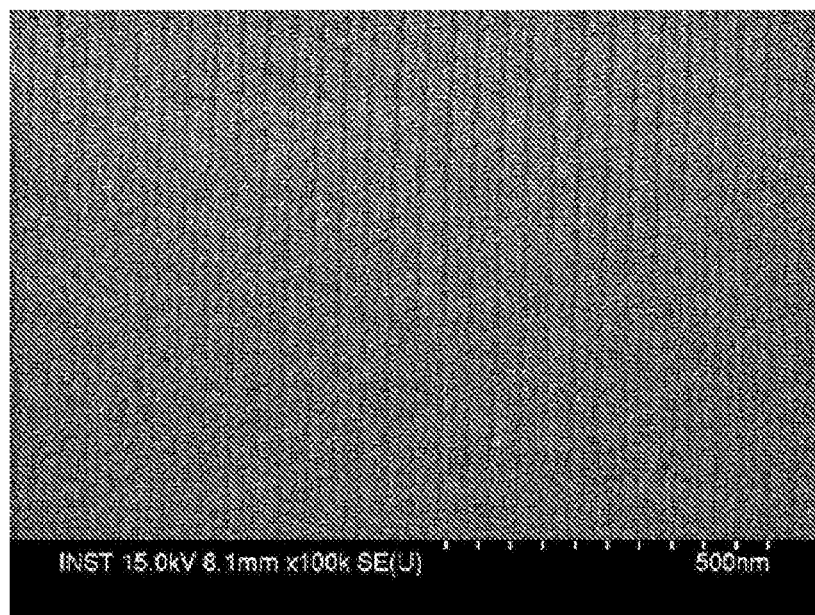


FIG. 27



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METHODS OF MANUFACTURING ABRASIVE PARTICLE AND POLISHING SLURRY

CROSS-REFERENCE TO RELATED APPLICATION

This application claims priority to Korean Patent Application No. 10-2013-0109872 filed on Sep. 12, 2013 and all the benefits accruing therefrom under 35 U.S.C. §119, the contents of which are incorporated by reference in their entirety.

BACKGROUND

The present disclosure relates to a method of manufacturing an abrasive particle, and more particularly, to methods of manufacturing an abrasive particle and a polishing slurry capable of enhancing the polishing rate of a target layer to be polished and decreasing micro scratches.

A chemical mechanical polishing (CMP) process is conducted by a polishing pad equipped in a polishing apparatus after a slurry containing abrasive particles is put on a substrate. In this regard, the abrasive particles mechanically polish a surface of the substrate with a pressure applied from the polishing apparatus, and chemical components contained in the slurry chemically react with the surface of the substrate to chemically remove a portion of the surface of the substrate. The abrasive particles may include, for example, ceria (CeO_2), and the like, and may be selectively used according to target layers to be polished.

Meanwhile, in existing methods of manufacturing a NAND flash memory, the shallow trench isolation (STI) process in which a nitride layer is used as a hard mask in order to form a device isolation layer is conducted. That is, a nitride layer is first formed on a substrate, a trench is formed on a predetermined region of the substrate, an oxide layer is formed to fill the trench, and the oxide layer is polished to form a device isolation layer. In this regard, the oxide is polished using a dry ceria slurry capable of securing a high polishing selection ratio of the oxide layer and the nitride layer until the nitride layer is exposed, and then the remaining nitride layer is removed by a wet etching. However, when the device scale is reduced to 20 nm or less, loss of the oxide layer occurs during the wet etching of the nitride layer and leakage current sharply increases between devices due to the loss of the oxide layer, so that the devices may be erroneously operated.

To solve the above-described problems, a new CMP process has been developed, which uses a polysilicon layer used as a floating gate as a polishing stop layer instead of using the nitride layer as a hard mask. That is, a tunnel insulating layer and a polysilicon layer are formed on a substrate, the polysilicon layer, the tunnel insulating layer and the substrate are sequentially etched to form a trench, an insulating layer is formed to fill the trench, and then the insulating layer is polished until the polysilicon layer is exposed, thereby forming a device isolation layer. Herein, when surface defects, particularly, micro scratches are generated in the polysilicon layer used as a floating gate after the CMP process, the generated micro scratches have an influence on the threshold voltage of devices. Then, since the dry ceria particles have an angular grain shape and a wide grain size distribution as shown in FIG. 1 due to limitations of the manufacturing method, the application of such dry ceria particles to the CMP process for forming NAND flash memory devices inevitably creates micro scratches. Compared with the dry ceria particles, since wet ceria particles have a relatively narrow grain

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size distribution, do not create particles having a large secondary particle diameter, and have a polyhedral structure as shown in FIG. 2, the wet ceria particles may greatly improve micro scratches compared with the dry ceria particles. However, when the size of the wet ceria particles is not larger than 40 nm, the polishing rate of the insulating layer is very low, and the size of the wet ceria particles is 100 nm or larger, the number of micro scratches is sharply increased due to sharp crystal faces of the polyhedral structure.

Meanwhile, U.S. Pat. Nos. 6,221,118 and 6,343,976 disclose a method of synthesizing a ceria particle used for polishing an insulating layer in a shallow trench isolation (STI) process, and a substrate polishing method using the same. The related arts also disclose an average particle diameter and a particle diameter distribution range of abrasive particles required for the characteristics of a slurry for polishing an insulating layer. However, since the ceria particles disclosed in the above-described related arts substantially include macro abrasive particles causing micro scratches, the ceria particles fail to suppress creation of micro scratches.

SUMMARY

The present disclosure provides methods of manufacturing an abrasive particle and a polishing slurry capable of enhancing the polishing ratio of a target layer to be polished and minimizing micro scratches.

The present disclosure also provides an abrasive particle and a polishing slurry capable of enhancing the polishing ratio of a target layer to be polished and minimizing micro scratches by decreasing sharp crystal faces of the abrasive particle having a polyhedral structure to the maximum extent.

The present disclosure also provides a method of manufacturing an abrasive particle capable of reducing sharp crystal faces by forming projection-shaped auxiliary particles on surfaces thereof having a polyhedral structure, and a polishing slurry.

In accordance with an exemplary embodiment, a method of manufacturing an abrasive particle, includes: mixing a first precursor material aqueous solution and a diluted alkaline solution and thermally treating the mixture solution to prepare a mother particle having a polyhedral crystal face; and adding an alkaline solution to a mixture solution in which the mother particle is mixed, mixing a second precursor material aqueous solution and thermally treating the resultant mixture solution to form a plurality of auxiliary particles protruded outward from a surface of the mother particle.

The plurality of auxiliary particles may be formed so as to cover a portion of each of crystal faces centered on an edge portion where at least three crystal faces among the polyhedral crystal faces meet.

The preparing of the mother particle may include: mixing a precursor material with deionized water to prepare the first precursor material aqueous solution; preparing a diluted alkaline solution and loading and stirring the prepared alkaline solution in a reaction container; mixing the first precursor material aqueous solution in the reaction container and thermally treating the resultant mixture solution; and cooling the thermally treated mixture solution.

The above method may further include mixing an acidic solution to the first precursor material aqueous solution.

The thermally treating may be conducted at a temperature higher than 60° C. and not higher than 100° C. for approximately 2 hours to approximately 24 hours.

The thermally treating temperature may rise at a rate of approximately 0.2° C./min to approximately 1° C./min.

The forming of the auxiliary particles may include: adding and stirring an alkaline solution in a mixture solution in which the mother particle is mixed; mixing the second precursor material aqueous solution prepared by mixing a precursor material with deionized water in the mixture solution in which the mother particle is mixed; thermally treating the mixture solution; and cooling the thermally treated mixture solution.

The thermally treating may be conducted at a temperature higher than 60° C. and not higher than 100° C. for approximately 2 hours to approximately 24 hours.

The thermally treating temperature may rise at a rate of approximately 0.2° C./min to approximately 1° C./min.

The above method may further include repeating the adjusting of the size of the auxiliary particles at least one time.

The adjusting of the size of the auxiliary particles may include: adding and stirring an alkaline solution in a mixture solution in which an abrasive particle including the mother particle and the auxiliary particles formed on the surface of the mother particle is mixed; mixing a third precursor material aqueous solution prepared by mixing a precursor material with deionized water in the mixture solution in which the abrasive particle is mixed; thermally treating the mixture solution; and cooling the thermally treated mixture solution.

The thermally treating may be conducted at a temperature higher than 60° C. and not higher than 100° C. for approximately 2 hours to approximately 24 hours.

The thermally treating temperature may rise at a rate of approximately 0.2° C./min to approximately 1° C./min.

The auxiliary particles adjacent to each other may be spaced apart from each other or contact each other.

The plurality of auxiliary particles contacting each other may have an overlapping height ranging from approximately 0% to approximately 70% to a maximum height thereof.

Each of the mother particle and the auxiliary particles may include a ceria particle.

The auxiliary particle to the mother particle may be formed at a size ratio of approximately 100:1 to approximately 5:1.

The abrasive particle may be formed to have an average particle diameter ranging from approximately 6 nm to approximately 350 nm.

The mother particle may have an average particle diameter of approximately 5 nm to approximately 300 nm and the auxiliary particle may have an average particle diameter of approximately 1 nm to approximately 50 nm.

In accordance with another exemplary embodiment, a method of manufacturing a polishing slurry polishing a workpiece, wherein an abrasive particle which polishes the workpiece and has a plurality of protrusions protruded outward is dispersed in a dispersing agent.

The abrasive particle may include polyhedral crystal faces, and the protrusion may be formed from an edge where at least two of the polyhedral crystal faces meet.

The auxiliary particle to the mother particle may be formed at a size ratio of approximately 100:1 to approximately 5:1.

The abrasive particle may be contained in an amount ranging from approximately 0.1 wt % to approximately 5 wt % based on a solid component.

The above method may further include adding a polishing accelerating agent, wherein the polishing accelerating agent may include a cationic low molecular weight polymer, a cationic high molecular weight polymer, a hydroxylic acid, and an amino acid, which convert a surface potential of the abrasive particle to a minus potential.

The polishing accelerating agent may be contained in an amount of approximately 0.01 wt % to approximately 0.1 wt % based on 1 wt % of the abrasive particle.

The cationic low molecular and high molecular polymers may include at least one of an oxalic acid, a citric acid, a polysulfonic acid, a polyacrylic acid, a polymethacrylic acid (Darvan C-N), copolymeric acids thereof, or salts thereof, the hydroxylic acid comprises at least one of a hydroxylbenzoic acid, an ascorbic acid, or salts thereof, and the amino acid comprises at least one of a picolinic acid, a glutaminic acid, a tryptophan acid, an aminobutylic acid, or salts thereof.

The above method may further include adding a pH adjusting agent adjusting pH of the slurry, wherein the pH of the slurry is maintained in a range of 4 to 9 by the pH adjusting agent.

BRIEF DESCRIPTION OF THE DRAWINGS

Exemplary embodiments can be understood in more detail from the following description taken in conjunction with the accompanying drawings, in which:

FIGS. 1 and 2 show photographs of existing dry and wet ceria abrasive particles and schematic views of polishing using these particles;

FIG. 3 is a schematic view of abrasive particles according to an embodiment of the present disclosure;

FIG. 4 is an enlarged schematic view of an abrasive particle in which adjacent auxiliary particles overlap;

FIGS. 5 and 6 are a flow diagram and a heat treatment condition diagram for explaining methods of manufacturing an abrasive particle according to embodiments of the present disclosure;

FIGS. 7 to 9 are schematic views and photographs of abrasive particles obtained by a manufacturing method according to an embodiment of the present disclosure;

FIG. 10 is photographs for comparison between existing dry and wet abrasive particles and abrasive particles of the present disclosure;

FIG. 11 shows a photograph of abrasive particles according to the present disclosure and a schematic view of polishing using the abrasive particles;

FIG. 12 is an XRD graph of existing dry and wet abrasive particles and abrasive particles of the present disclosure;

FIGS. 13 and 14 are a graph and a photograph showing a size distribution of auxiliary particles according to temperature in the course of temperature rise to a heat treatment temperature of the present disclosure;

FIGS. 15 to 17 are a graph and a photograph showing a size distribution of auxiliary particles according to heat treatment temperature of the present disclosure;

FIGS. 18 to 20 are cross-sectional views illustrating a method of manufacturing a semiconductor device by using a polishing slurry containing abrasive particles according to an embodiment of the present disclosure;

FIGS. 21 and 22 are photographs of abrasive particles according to comparative examples and inventive examples;

FIG. 23 is a graph showing a particle diameter distribution of abrasive particles manufactured according to Inventive Examples;

FIGS. 24 and 25 are photographs of sections of substrates after the substrates are subject to CMP processes by using slurries containing abrasive particles according to a comparative example and an example of the present disclosure; and

FIGS. 26 and 27 are photographs of surfaces of polishing stop layers after substrates are subject to CMP processes by using slurries containing abrasive particles according to Comparative Example and Inventive Example.

DETAILED DESCRIPTION OF EMBODIMENTS

Hereinafter, exemplary embodiments will be described in detail with reference to the accompanying drawings. The present disclosure may, however, be embodied in many different forms and should not be construed as being limited to the embodiments set forth herein; rather, these embodiments are provided so that this disclosure will be thorough and complete, and will fully convey the concept of the invention to those skilled in the art. Further, the present disclosure is only defined by scopes of claims.

FIG. 3 is a schematic view of abrasive particles according to an embodiment of the present disclosure;

Referring to FIG. 3, an abrasive particle according to an embodiment of the present disclosure includes a mother particle 10, and a plurality of auxiliary particles 20 provided to a surface of the mother particle 10.

The mother particle 10 may include particles, such as ceria (CeO_2), and the like. Also, the mother particle 10 may be analyzed through an XRD measurement, and has the same crystal structure as the wet ceria and has polyhedral crystal faces. Also, the mother particle 10 may be provided in an average particle diameter ranging from 5 nm to 300 nm, preferably ranging from 20 nm to 100 nm, and more preferably ranging from 40 nm to 70 nm. When the average particle diameter of the mother particle 10 is so small, the target layer to be polished is not easily polished so that the polishing rate is reduced, and when the average particle diameter of the mother particle 10 is so large, the mother particle 10 is again grown up to a polyhedral structure to generate micro scratches in the polishing stop layer. Therefore, the mother particle 10 may have an average particle diameter in such a range that does not reduce the polishing rate of the target layer to be polished and does not generate micro scratches in the polishing stop layer.

The auxiliary particle 20 is formed in plurality on a surface of the mother particle 10, and may be formed protruding outward from a plurality of edge portions of the mother particle 10. That is, the auxiliary particles 20 may be formed so as to cover at least a portion of each crystal face from an edge portion where at least three crystal faces meet. The auxiliary particle 20 may include ceria (CeO_2), and the like. That is, the auxiliary particle 20 may be formed of the same material as the mother particle 10, or a material that is not the same as the mother particle 10, and it is preferable that the auxiliary particle 20 be formed of the same material as the mother particle 10. In this regard, the auxiliary particles 20 may be grown in various sizes depending on the growing conditions, such as the size of the mother particle 10, growing time, growing temperature, and the like, and the adjacent auxiliary particles 20 may be formed spaced apart from each other as shown in FIG. 3A or contacting each other as shown in FIG. 3B. Also, in case the auxiliary particles 20 contact each other, the auxiliary particles 20 are grown up on faces between edges of the mother particle 10 according to the growing time of the auxiliary particles 20, so that the adjacent auxiliary particles 20 may overlap each other. In this regard, in case the adjacent auxiliary particles 20 overlap each other, the overlapping portions of the auxiliary particles 20 are formed with a height (d2) greater than 0 and less than 70 when it is assumed that the maximum height (d1) of the auxiliary particles 20 is 100 as shown in FIG. 4. That is, the overlapping portions of the auxiliary particles 20 may be formed with a height between 0 and 70% with respect to the maximum height of the auxiliary particles 20 which is the farthest distance of the auxiliary particles 20 from the surface of the mother particle 10. In this regard, when the overlapping por-

tions of the auxiliary particles 20 are too high, the abrasive particle becomes too large and is again grown up to a polyhedral structure, so that the abrasive particle may cause occurrence of micro scratch in the polishing stop layer. Meanwhile, these auxiliary particles 20 may be formed in a size ratio ranging from 1:300 to 1:5 with respect to the size of the mother particle 10. For example, when the mother particle 10 is provided with an average particle diameter ranging from 5 nm to 300 nm, the auxiliary particles 20 may be provided with an average particle diameter ranging from 1 nm to 50 nm, preferably from 3 nm to 20 nm, and more preferably from 5 nm to 10 nm. That is, the particle diameter of one auxiliary particle 20 may be defined as a distance from the surface of the mother particle 10 to the farthest distance of the corresponding auxiliary particle 20, and the average particle diameter of the auxiliary particles 20 defined thus may be provided in a range of 1 nm to 50 nm. Then, when the average particle diameter of the auxiliary particles 20 is too small, the auxiliary particles 20 fail to reduce the sharpness of the crystal faces of the mother particle 10 and thus fail to prevent occurrence of micro scratches in the polishing stop layer, and when the average particle diameter of the auxiliary particles 20 is too large, the auxiliary particles 20 are again grown up to a polyhedral structure surrounding the mother particle 10, so that the auxiliary particles 20 may cause occurrence of micro scratches in the polishing stop layer. Accordingly, the abrasive particle according to an embodiment of the present disclosure may be provided with an average particle diameter from one auxiliary particle 20 to another auxiliary particle 20 through the mother particle 10 ranging from 6 nm to 350 nm, preferably from 20 nm to 150 nm, and more preferably from 40 nm to 80 nm. That is, the distance between the auxiliary particles 20 that are farthest away from each other through the mother particle 10 may be in a range of 6 nm to 350 nm.

Methods of manufacturing an abrasive particle according to embodiments of the present disclosure will be described with reference to FIGS. 5 and 6. FIG. 5 is a flow diagram showing methods of manufacturing an abrasive particle according to embodiments of the present disclosure, and FIG. 6 is a conditional view of heat treatment time and temperature. Also, FIGS. 7 and 9 are schematic views and photographs of abrasive particles obtained by a manufacturing method according to an embodiment of the present disclosure.

Referring to FIGS. 5 and 6, a method of manufacturing an abrasive particle according to an embodiment of the present disclosure may include preparing (S100) a mother particle, and forming (S200) auxiliary particles on a surface of the mother particle. The method of manufacturing an abrasive particle may further include increasing (S300) the size of the auxiliary particles. While the abrasive particle in related arts is manufactured by a solid phase reaction method and is then pulverized to a proper size for the use thereof, the abrasive particle according to an embodiment of the present disclosure is manufactured by a wet chemical synthesis method.

Hereinbelow, the forming (S100) of preparing a mother particle will be described. First, a precursor, for example, a cerium aqueous solution is prepared by mixing a cerium salt with deionized water. The cerium salt and the deionized water may be mixed at a ratio of, for example, 2:1 to 4:1. The cerium salt used herein may be at least one of Ce(III) salt and Ce(IV) salt. That is, at least one Ce(III) salt may be mixed with deionized water, at least one Ce(IV) salt may be mixed with deionized water, or Ce(III) salt and Ce(IV) salt may be mixed with deionized water. The Ce(III) salt may include cerium chloride, cerium bromide, cerium nitrate, acetate cerium chloride, and the like, and the Ce(IV) salt may include cerium ammonium nitrate, cerium sulfate, and the like. Preferably,

the Ce(III) salt may be cerium nitrate, and the Ce(IV) salt may be cerium ammonium nitrate. Meanwhile, in order to stabilize the cerium aqueous solution prepared by mixing cerium salt with deionized water, an acid solution may be mixed. The acid solution and the cerium aqueous solution may be mixed at a ratio of 1:1 to 1:100. The acid solution may include oxygenated water, a nitric acid, an acetic acid, a hydrochloric acid, a sulfuric acid, and the like. The pH of the cerium aqueous solution mixed with the acidic solution may be adjusted to, for example, 0.01. Separately from the cerium aqueous solution, an alkaline solution is prepared. The alkaline solution may be prepared by mixing ammonia, sodium hydrate, potassium hydrate, or the like with deionized water and diluting the mixture to a proper concentration. In this regard, the alkaline material and deionized water may be diluted at a ratio of 1:1 to 1:100, and the pH of the mixture solution may be, for example, 12.3. The alkaline solution diluted thus is loaded in a reaction container and then stirred, for example, for a time not more than 5 hours in an atmosphere of inert gas, such as nitrogen, argon, helium, or the like. The cerium aqueous solution is added in the reaction container in which the diluted alkaline solution is loaded and is mixed with the alkaline solution, for example, at a rate of 0.1 l per second. At this time, the pH of the mixture solution may be, for example, 9.58. Then, the mixture solution is thermally treated at a predetermined temperature. The thermal treatment temperature may be 100° C. or lower—for example, a temperature exceeding 60° C. and not higher than 100° C., and the heat treatment time may be 24 hours or less—for example, 1 hour to 24 hours. Also, the temperature rise rate from room temperature to the thermal treatment temperature may be in a range of 0.2° C./min to 1° C./min—for example, 0.5° C./min. The mixture solution which has undergone the heat treatment is cooled to 60° C. or lower, for example, within 2 hours. Through the above processes, a mixture solution in which the mother particle **10** having a particle diameter of 80 nm or less is mixed is prepared. That is, the mother particle is formed in a polyhedral structure having sharp crystal faces without any auxiliary particles on a surface thereof as shown in the schematic view of FIG. 7A and the photograph of FIG. 7B.

Next, the growing (S200) of auxiliary particles on a surface of the mother particle will be described. In a state that the atmosphere of inert gas is maintained, the alkaline solution is further added in the mixture solution in which the mother particle **10** is mixed and then stirring is performed for a time of 5 hours or less. In this regard, the alkaline solution may be, for example, ammonia that is not diluted by deionized water. A cerium aqueous solution prepared by mixing cerium salt with deionized water at a mixing ratio of 2:1 to 4:1 is mixed with the mixture solution in which the mother particle **10** is mixed, and the resultant solution is then heated at a temperature of 100° C. or lower, for example, at a temperature exceeding 60° C. and not higher than 100° C. to perform heat treatment for a time of 24 hours or less. In this regard, the temperature of the mixture solution may rise from, for example, room temperature to 40° C., to a heat treatment temperature at a temperature rise rate of 0.2° C./min to 1° C./min. The mixture solution which has undergone the heat treatment for 24 hours or less is cooled to 60° C. or less within 2 hours. Through the above processes, a abrasive particle having a plurality of auxiliary particles **20** formed on the surface of the mother particle **10** and having a primary particle diameter of 90 nm or less is formed as shown in the schematic view of FIG. 8A and the photograph of FIG. 8B. Meanwhile, the auxiliary particle **20** may be grown and formed to a predetermined size after a nucleus is formed on

the surface of the mother particle **10**. That is, the auxiliary particle is grown after nucleus is formed in the course of temperature rise to the heat treatment temperature. For example, when the heat treatment is conducted at a temperature of 80° C., nucleus of the auxiliary particle **20** is formed on the surface of the mother particle **10** at temperatures rising to 60° C., and is grown during a temperature rise period from 60° C. to 80° C., so that the auxiliary particle **20** having a predetermined size is formed. After the auxiliary particle **20** is formed on the surface of the mother particle **10**, the auxiliary particle **20** is rigidly bonded to the surface of the mother particle **10** by a heat treatment within 24 hours. That is, the bonding force between the mother particle **10** and the auxiliary particle **20** may be adjusted according to the heat treatment time. For example, when the heat treatment time is lengthened, the bonding force between the mother particle **10** and the auxiliary particle **20** increases, and when the heat treatment time is shortened, the bonding force between the mother particle **10** and the auxiliary particle **20** decreases. When the bonding force between the mother particle **10** and the auxiliary particles **20** is weak, the auxiliary particles **20** may be detached from the mother particle **10** during the polishing process. Therefore, it is preferable that the heat treatment be conducted for a sufficient time such that the mother particle **10** and the auxiliary particles **20** strongly bond to each other. However, when the heat treatment time is too long, since the productivity is reduced, it is preferable that the heat treatment time be within 2 hours to 24 hours. Also, the size of the auxiliary particles **20** may be adjusted according to the heat treatment temperature. That is, when the heat treatment temperature is high, the size of the auxiliary particles **20** may increase. For example, at a temperature of 60° C., the nucleus of the auxiliary particle **20** is formed but is not grown, so that the size of the auxiliary particle **20** is not increased, and at a temperature above 60° C., the nucleus is grown, so that the size of the auxiliary particle **20** abruptly increases as the temperature rises. However, when the heat treatment temperature is too high, the size of the auxiliary particles **20** becomes too large, so that a new mother particle **10** may be formed. Therefore, it is preferable that the heat treatment be conducted at a temperature higher than 60° C. and not higher than 100° C.

In order to grow the size of the auxiliary particles **20** formed on the surface of the mother particle **10**, the growing process of the auxiliary particles **20** may be conducted at least one time (S300). For example, in a state that the atmosphere of inert gas is maintained, the alkaline solution is further added to the mixture solution in which the abrasive particle the mother particle **10** and the auxiliary particles **20** formed on the surface of the mother particle **10** is mixed, and stirring is conducted for a time of 5 hours or less, and a cerium aqueous solution is prepared by mixing cerium and deionized water at a mixing ratio of 2:1 to 4:1, and is then heated from room temperature to 40° C. to a temperature of 100° C. or lower at a temperature rise rate of 0.2° C./min to 1° C./min to perform heat treatment for a time of 24 hours or less. The mixture solution which has been subject to the heat treatment is cooled to room temperature within 2 hours. Through the above processes, a abrasive particle having a plurality of auxiliary particles **20** formed on the surface of the mother particle **10** and having a primary particle diameter of 100 nm or less is formed as shown in the schematic view of FIG. 9A and the photograph of FIG. 9B. That is, by repeating the growing process of the auxiliary particles **20**, the size of the auxiliary particles **20** increases, so that the auxiliary particles **20** contact each other or overlap each other.

As described above, in the case of the mother particle, when the mixture solution of the precursor aqueous solution and the diluted alkaline solution is heated at a proper temperature rise rate in a proper heat treatment temperature range, the cerium salt in the mixture solution reacts to create a fine nucleus of ceria, i.e., cerium oxide (e.g., CeO_2 , Ce_2O_3), and a crystal is grown from the fine nucleus and is manufactured to a crystal particle having a few nm to a few hundred nm. The crystal nucleation is mainly performed in an initial temperature rise period, and the crystal growth is mainly conducted in a next temperature rise period. Also, in the case of the auxiliary particle, when a solution containing a cerium salt is added to a solution containing the mother particle and the mixture solution is heated at a proper temperature rise rate to a proper temperature, the cerium salt is attached on a surface of the mother particle in the course of temperature rise to create a nucleus of the auxiliary particle, and the nucleus of the auxiliary particle is grown and is then manufactured to the auxiliary crystal particle. At this time, similarly to the manufacturing of the mother particle, the crystal nucleation is mainly performed in an initial temperature rise period, and the crystal growth is mainly performed in a next temperature rise period. Also, since the nucleus of the auxiliary particle is preferentially created on an edge where crystal faces of the mother particle meet, the auxiliary particle is grown centered on the edge of the mother particle.

As described above, the photographs of the abrasive particle including the mother particle **10** and the auxiliary particles **20** formed on the surface of the mother particle **10** according to the present disclosure and the existing dry and wet ceria particles are shown in FIG. **10** for comparison of shape. That is, FIGS. **10A** and **10B** are photographs of the existing dry and wet ceria particles and FIG. **10C** is the photograph of the abrasive particle according to the present disclosure. As shown in FIG. **10A**, since the dry ceria particle is angular in shape of crystal particle and has a wide particle diameter distribution, the application of the dry ceria particle to the CMP process for NAND flash memory devices inevitably generates micro scratches in the polysilicon layer as shown in FIG. **1**. Also, as shown in FIG. **10B**, since the wet ceria particle has a polyhedral structure and is large in size, the application of the wet ceria particle to the CMP process for NAND flash memory devices inevitably generates micro scratches in the polysilicon layer as shown in FIG. **2**. However, as shown in FIG. **10C**, since the abrasive particle according to the present disclosure is small in size and does not have sharp crystal faces compared with the existing wet ceria particle, although the abrasive particle is applied to the CMP process for NAND flash memory devices as shown in FIG. **11**, a micro scratch is not generated in the polishing layer. Also, as seen from the XRD graph of FIG. **12**, the ceria abrasive particle according to the present disclosure has almost the same crystallinity as the existing dry and wet ceria particles. Therefore, it may be understood that the ceria abrasive particle according to the present disclosure has a strength that may be used as an abrasive particle in a CMP process for planarizing a device isolation layer.

FIG. **13** is a graph showing a size distribution of auxiliary particles according to temperature in the course of temperature rise to a heat treatment temperature, and FIG. **14** shows photographs of abrasive particles at respective temperatures. As shown in FIGS. **13** and **14**, the average particle diameter of the auxiliary particles at 30° C. is about 3.661 nm, the average particle diameter of the auxiliary particles at 40° C. is about 3.717 nm, the average particle diameter of the auxiliary particles at 50° C. is about 3.718 nm, and the average particle diameter of the auxiliary particles at 60° C. is about 3.574 nm

That is, although the temperature rises from 30° C. to 60° C., the auxiliary particles **20** are not almost grown. This is because the nucleus of the auxiliary particle **20** is created but is not further grown. However, when the temperature exceeds 60° C., the average particle diameter of the auxiliary particle **20** is abruptly grown, and when the temperature rises to 70° C., the average particle diameter of the auxiliary particle **20** increases to 14.632 nm, and when the temperature rises to 80° C., the average particle diameter of the auxiliary particle **20** increases to 20.843 nm. This is because the nucleus of the auxiliary particle **20** is abruptly grown from the temperature exceeding 60° C. Therefore, in the case of the abrasive particle according to the present disclosure, it may be seen that the size of the auxiliary particle **20** abruptly increases in a predetermined temperature range in the course of temperature rise.

FIGS. **15** and **17** are a graph and a photograph showing a size distribution of auxiliary particles according to heat treatment temperature of the present disclosure. That is, FIG. **15** shows the size of the auxiliary particle when the heat treatment is performed at 60° C., FIG. **16** shows the size of the auxiliary particle when the heat treatment is performed at 70° C., and FIG. **17** shows the size of the auxiliary particle when the heat treatment is performed at 80° C. As shown in FIG. **15**, when the heat treatment is performed at 60° C., the auxiliary particle has a size distribution in a range of about 9 nm to about 17 nm, and has a maximum distribution at about 12 nm. Also, in this case, the average particle diameter of the auxiliary particle is about 11.833 nm. As shown in FIG. **16**, when the heat treatment is performed at 70° C., the auxiliary particle has a size distribution in a range of about 7 nm to about 18 nm, and has a maximum distribution at about 11 nm. Also, in this case, the average particle diameter of the auxiliary particle is about 12.375 nm. As shown in FIG. **17**, when the heat treatment is performed at 80° C., the auxiliary particle has a size distribution in a range of about 14 nm to about 35 nm, and has a maximum distribution at about 23 nm. Also, in this case, the average particle diameter of the auxiliary particle is about 24.533 nm. It may be seen from these results that when the heat treatment temperature is high, the size of the auxiliary particle increases and the auxiliary particle has a wide size distribution.

A polishing slurry may be manufactured by mixing, in a dispersing agent, the abrasive particles including the mother particle **10** and the plurality of auxiliary particles **20** formed on the surface of the mother particle **10** and manufactured by the above-described method. Also, a polishing accelerating agent, a pH adjusting agent, and the like may be further mixed.

The abrasive particle includes a ceria mother particle and a plurality of ceria auxiliary particles formed on a surface of the ceria mother particle as described above, and may be contained in an amount of 0.1 wt % to 5 wt % and preferably 0.25 wt % to 2 wt % in the polishing slurry based on the solid component. In this regard, when the abrasive particle is contained in an amount of 0.1 wt % or less, the polishing rate is too low, and when the abrasive particle is contained in an amount of 5 wt % or more, the polishing rate is too high, so that a target layer to be polished may be overpolished.

The polishing accelerating agent may include an cationic low molecular polymer, an cationic high molecular polymer, a hydroxylic acid, or an amino acid that may convert the surface potential of the abrasive particle to minus potential. For example, the cationic low molecular and high molecular polymers may include at least one of an oxalic acid, a citric acid, a polysulfonic acid, a polyacrylic acid, a polymethacrylic acid (Darvan C-N), copolymeric acids thereof, or

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salts thereof. Also, the hydroxylic acid may include at least one of a hydroxylbenzoic acid, an ascorbic acid, or salts thereof. The amino acid may include at least one of a picolinic acid, a glutaminic acid, a tryptophan acid, an aminobutylic acid, or salts thereof. The polishing accelerating agent may be contained in an amount of 0.01 wt % to 0.1 wt %, and preferably 0.02 wt % to 0.06 wt % based on 1 wt % of the abrasive particle. When the amount of the polishing accelerating agent is less than 0.01 wt % based on the weight of the abrasive particle, the dispersion stability is deteriorated, and when the amount of the polishing accelerating agent exceeds 0.1 wt %, the polishing of the target layer to be polished may be suppressed. Therefore, the weight percentage of the polishing accelerating agent may be adjusted such that the dispersion stability is enhanced and the polishing is not suppressed.

The pH of the polishing slurry may be adjusted to 4 to 9, preferably 5 to 9 by using a pH adjusting agent. When the pH of the polishing slurry is 4 or less, the dispersion stability is deteriorated, and when the pH of the polishing slurry is 9 or higher, the polishing rate of the polishing stop layer, for example, the polysilicon layer sharply increases due to strong alkalinity.

As described above, since the abrasive particle according to an embodiment of the present disclosure is provided with the plurality of auxiliary particles 20 formed on the surface of the mother particle 10, the abrasive particle may decrease the sharp crystal faces of the mother particle 10 to the maximum extent. Therefore, the abrasive particle may suppress the occurrence of micro scratches in the polishing stop layer, for example, the polysilicon layer underlying the target layer to be polished to the maximum extent, thereby enhancing the device reliability and productivity. A method of manufacturing a semiconductor device by using the polishing slurry containing abrasive particles according to an embodiment of the present disclosure will be described with reference to FIGS. 18 to 20.

Referring to FIG. 18, a tunnel insulating layer 110 is formed on a substrate 100 and a conductive layer 120 is then formed on the tunnel insulating layer 110. The substrate 100 may be selected from various substrates used in manufacturing semiconductor devices, and may be, for example, a silicon substrate. The tunnel insulating layer 110 may be formed by using an oxide layer (SiO_2), a nitride layer (Si_3N_4), or the like, and may be formed in a single layer structure or a structure having at least two layers. In this regard, the insulating layer 110 may be formed in a thickness that enables tunneling of carriers. Also, the conductive layer 120 may be used as a floating gate of a NAND flash memory device, and may be formed by using a polysilicon layer.

Referring to FIG. 19, predetermine regions of the conductive layer 120, the tunnel insulating layer 110 and the substrate 100 are etched to a predetermined depth of the substrate 100 to form a plurality of trenches. An insulating layer 130 is formed such that the trenches are filled. The insulating layer 130 may be formed of an oxide-based material, for example, at least one of a borophosphosilicate glass (BPSG) layer, a phosphosilicate glass (PSG) layer, a high density plasma (HDP) layer, a tetra ethyl ortho silicate (TEOS) layer, an undoped silica glass (USG) layer, a plasma enhanced tetra ethyl ortho silicate glass (PETEOS) layer, and a high aspect ratio process (HARP) layer. Also, the insulating layer 130 may be formed by a physical vapor deposition (PVD) method, a chemical vapor deposition (CVD) method, a metal organic chemical vapor deposition (MOCVD) method, an atomic layer deposition (ALD) method, or an AL-CVD method in which the CVD method and the ALD method are combined. Meanwhile, a liner oxide layer may be formed on

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inner side surfaces of the trenches by oxidizing the substrate 100 prior to filling the trenches with the insulating layer 130.

Referring to FIG. 20, the substrate 100 in which the insulating layer 130 is filled in the trenches is loaded in a CMP apparatus and then the insulating layer 130 is polished by using a polishing slurry containing the abrasive particles according to an embodiment of the present disclosure. That is, the insulating layer 130 is polished by using a polishing pad of a polishing apparatus and the polishing slurry until the conductive layer 120 is exposed. Also, for sufficient polishing, the polishing may be further conducted for a predetermined time after the conductive layer 120 is exposed. In this regard, the polishing selection ratio of the insulating layer 130 to the conductive layer 120 is 10:1 to 50:1. Thus, a plurality of device isolation layers 140 are formed between the conductive layers 120.

Although not shown in the drawings, a second conductive layer, such as a polysilicon layer or the like may be formed on the substrate in which the device isolation layers are formed, and then patterned to form a floating gate, and a dielectric layer and a third conductive layer may be formed on the resultant substrate and then patterned to form a control gate. Thus, a NAND flash memory device in which the floating gate and the control gate are stacked may be manufactured.

Example

Manufacturing of Abrasive Particle

An abrasive particle including a mother particle and a plurality of auxiliary particles formed on a surface of the mother particle according to an embodiment of the present disclosure was manufactured as follows. A cerium(III) salt and deionized water were mixed at a mixing ratio of 2:1 to 4:1—for example, 1 kg to 4 kg of cerium(III) salt and 0.25 kg to 2 kg of deionized water to prepare a cerium(III) aqueous solution, and a cerium(IV) salt and deionized water were mixed at a mixing ratio of 1:500 to 1:3000—for example, 1 g to 3 g of cerium(IV) salt and 0.5 kg to 9 kg of deionized water to prepare a cerium(IV) aqueous solution. The cerium(IV) aqueous solution and a nitric acid were mixed at a mixing ratio of 1:1 to 100:1—for example, 1 kg to 5 kg of the cerium(IV) solution and 0.1 kg to 5 kg of the nitric acid, to prepare a cerium(IV) mixture solution. Also, the cerium(III) aqueous solution and the cerium(IV) mixture solution were mixed to prepare a cerium mixture solution. Further, ammonia and deionized water were loaded at a mixing ratio of 1:2 to 1:10—for example, 1 kg to 5 kg of ammonia and 1 kg to 50 kg of deionized water in a reaction container in an inert atmosphere and then stirred to prepare an alkaline aqueous solution. In a state that the cerium mixture solution was put in the reaction container and then stirred while maintaining the inert atmosphere, the cerium mixture solution was heated from room temperature to 100° C. or lower—for example, 70° C. to 90° C. to perform a heat treatment for a time period of 8 hours or less—for example, 1 hour to 4 hours. By performing the heat treatment as above, a mother particle mixture solution in which a protrusion is not introduced on a surface thereof was prepared.

Thereafter, the ceria particle mixture solution was cooled to a temperature of 60° C. or lower—for example, 20° C. to 40° C., and the ceria particle mixture solution and ammonia were put in a reaction container, mixed at a mixing ratio of 10:1 to 2:1—for example, 8 kg to 100 kg of the ceria particle mixture solution and 10 kg to 4 kg of ammonia, and then stirred for a few minutes to a few ten minutes in an inert atmosphere. Then, a secondary cerium mixture solution in

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which 1 kg to 4 kg of a cerium(III) salt, 1 kg to 4 kg of a cerium(IV) salt, 1 kg to 9 kg of deionized water and 0.1 kg to 5 kg of a nitric acid were mixed was added to the ceria mixture solution to which ammonia was added, stirred, and heated to 100° C. or lower—for example, 70° C. to 90° C. to perform a heat treatment for 8 hours or less—for example, 1 hour to 4 hours. By completing the heat treatment as above, a particle mixture solution in which a primary auxiliary particle having a projection shape is formed on a surface of the mother particle was prepared.

Thereafter, the ceria particle mixture solution in which the primary auxiliary particle is formed was cooled to a temperature of 60° C. or lower—for example, 20° C. to 40° C., and the ceria particle mixture solution and ammonia were put in a reaction container, mixed at a mixing ratio of 10:1 to 2:1—for example, 8 kg to 100 kg of the ceria particle mixture solution and 10 kg to 4 kg of ammonia, and then stirred for a few minutes to a few ten minutes in an inert atmosphere. Then, a tertiary cerium mixture solution in which 1 kg to 4 kg of a cerium(III) salt, 1 kg to 4 kg of a cerium(IV) salt, 1 kg to 9 kg of deionized water and 0.1 kg to 5 kg of a nitric acid were mixed was added to the ceria mixture solution to which ammonia was added, stirred, and heated to 100° C. or lower—for example, 70° C. to 90° C. to perform a heat treatment for 8 hours or less—for example, for 1 hour to 4 hours. By completing the heat treatment as above, a particle mixture solution in which a secondary auxiliary particle having a projection shape is formed on a surface of the mother particle was prepared.

The particle mixture solution in which the secondary auxiliary particle is formed on the surface of the mother particle was cooled to room temperature to adjust pH of the mixture solution to an acidic pH of 4 or less, thereby completing the reaction. The mixture solution of which reaction was completed was left in room temperature to deposit the ceria particles having projections on a surface thereof, then deposition and washing using deionized water were repeated a few times, and then centrifugation of the mixture solution was performed to finally obtain particles.

Comparison Between Example and Comparative Example

Deionized water was added to a ceria suspension containing ceria abrasive particles having sharp crystal faces of a polyhedral structure according to Comparative Example to dilute the ceria suspension, and a nitric acid (HNO₃) or ammonia (NH₄OH) was added to adjust the pH of the ceria suspension to 4, 5, and 6. These resultant solutions were sufficiently stirred to prepare polishing slurries according to comparative examples.

Also, deionized water was added to a ceria suspension containing ceria abrasive particles having a plurality of auxiliary particles formed on a surface of the mother particle manufactured by the above-described method to dilute the ceria suspension, and Darvan C-N was added and then a nitric acid (HNO₃) or ammonia (NH₄OH) was added to adjust the pH of the ceria suspension to 4, 5, and 6. These resultant solutions were sufficiently stirred and then ultrasonicated to prepare polishing slurries according to Inventive Examples.

Then, polishing processes were conducted by using the polishing slurries according to Comparative Examples and the polishing slurries. POLI-300 (G&P) was used as a polishing apparatus, and IC 1000/Suba IV CMP pad (Dow chemical) was used as a polishing pad. Also, the falling pressure of the polishing pad was set to 6 psi and the rotational speeds of a table and a spindle were all set to 70 rpm. Under

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such conditions, the polishing slurries according to Comparative Examples and Examples were supplied at a flow rate of 100 ml/min to polish a 250 nm thick PETEOS layer formed on a 75 nm thick polysilicon layer for 60 seconds. The polishing results according to Comparative Examples and Examples are shown in Table 1. Also, the shapes of the abrasive particles according to Comparative Examples and Examples are shown in the photographs of FIG. 22. FIG. 23 is a graph showing size distributions of the mother particle manufactured according to an embodiment, a particle including primary auxiliary particles, and a particle having secondary auxiliary particles.

TABLE 1

	Comparative Example	Example
Shape	Polyhedron	Nano embossing
Primary particle diameter (nm)	78.58	77.25
Secondary particle diameter (nm)	157.5	157.4
Zeta Potential (mV)	46.58	-50.02
PETEOS polishing rate (Å/min)	1131	1531
Adding of Polysilicon	Polishing rate of PETEOS (Å/min)	472
Stop additive	Polishing rate of Polysilicon (Å/min)	680
	<20	<20
Thickness of Residual Polysilicon (nm)	74.4 ± 0.9	73.8 ± 1.4

First, as shown in FIG. 21, it may be seen that the abrasive particles according to Comparative Examples have a polyhedral structure and sharp crystal faces. However, as shown in FIG. 22, it can be seen that the abrasive particles according to Examples of the present disclosure have a nano-embossing structure in which projection-shaped auxiliary particles are formed on a surface of the mother particle. Also, as shown in FIG. 23, the mother particle (A) has a size distribution in a range of about 12 nm to about 150 nm, and has a maximum distribution at about 32.68 nm. The particle (B) including primary auxiliary particles has a size distribution in a range of about 8 nm to about 150 nm, and has a maximum distribution at about 54.36 nm. Also, the particle (C) including secondary auxiliary particles has a size distribution in a range of about 17 nm to about 150 nm, and has a maximum distribution at about 77.25 nm. Meanwhile, as shown in Table 1, the ceria abrasive particles having the polyhedral structure according to Comparative Examples and the ceria abrasive particles having the nano embossing structure according to Inventive Examples have almost similar primary and secondary particle diameters. That is, the abrasive particles according to Comparative Examples have a primary particle diameter of 78.58 nm and a secondary particle diameter of 157.5 nm, and the abrasive particles according to Inventive Examples have a primary particle diameter of 77.25 nm and a secondary particle diameter of 157.4 nm. Herein, the primary particle diameter indicates an average particle diameter of the ceria abrasive particles, and the secondary particle diameter indicates an average particle diameter when the ceria particles are mixed in the slurry. However, the ceria abrasive particles according to Comparative Examples have a surface Zeta potential of 46.58 mV, and the ceria abrasive particles according to Examples have a surface Zeta potential of -50.02 mV that is opposite in polarity to the surface Zeta potential of Comparative Examples. Also, in case of oxides, the polishing rate of the slurry according to Comparative Examples was 1,131 Å/min, and the polishing rate of the slurry according to Inventive Examples was 1,531 Å/min, and it can be seen from

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these results that the polishing rate of the inventive slurry is more excellent than that of the slurry according to Comparative Examples. Also, even in case a polysilicon polishing stop additive was added, the oxide polishing rate of the slurry according to Inventive Examples was 680 Å/min and the oxide polishing rate of the slurry according to Comparative Example was 472 Å/min, and it can be seen from these results that the polishing rate of the inventive slurry is more excellent than that of the slurry according to Comparative Examples. Meanwhile, from comparison results of TEM images after pattern CMP shown in FIGS. 24 and 25, it may be seen that there are no remarkable differences in dishing, thickness of residual polysilicon, or the like. However, in the case of the ceria slurry according to Comparative Example, many micro scratches viewed as stain occurred as shown in FIG. 26, but in the case of the ceria slurry according to Inventive Example, micro scratches did not occur in a polysilicon layer as shown in FIG. 27. Resultantly, compared with the ceria abrasive particles according to Comparative Examples, the ceria abrasive particles according to Inventive Example may enhance the polishing rate of oxides as well as decreasing the occurrence of micro scratches in the underlying polysilicon layer.

According to the embodiments of the present disclosure, since the abrasive particle includes a mother particle having a polyhedral structure, and a plurality of auxiliary particles provided on a surface of the mother particle, the abrasive particle may decrease sharp crystal faces of the mother particle to the maximum extent. Also, a polishing slurry may be manufactured by using such abrasive particles, and the manufactured polishing slurry may be used to polish an upper oxide-based material layer in a process of manufacturing 20 nm or less NAND flash memory devices in which a polysilicon layer used as a floating gate is used as a polishing stop layer.

Therefore, the occurrence of micro scratches in the polysilicon layer underlying the target layer to be polished may be suppressed to the maximum extent, and thus a change in threshold voltage may be prevented, thereby enhancing the device reliability. Furthermore, the polishing rate of an oxide layer may be improved and the polishing selection ratio of an oxide layer and a polysilicon layer may be improved, thus decreasing the polishing process time to enhance the productivity.

Although the abrasive particle, the polishing slurry, and the method of manufacturing a semiconductor device using the same have been described with reference to the specific embodiments, they are not limited thereto. Therefore, it will be readily understood by those skilled in the art that various modifications and changes can be made thereto without departing from the spirit and scope of the present invention defined by the appended claims.

What is claimed is:

1. A method of manufacturing an abrasive particle, comprising:

mixing a first precursor material aqueous solution and a diluted alkaline solution and thermally treating the mixture solution to prepare a mother particle having a polyhedral crystal face; and

adding an alkaline solution to a mixture solution in which the mother particle is mixed, mixing a second precursor material aqueous solution and thermally treating the resultant mixture solution to form a plurality of auxiliary particles protruded outward from a surface of the mother particle.

2. The method of claim 1, wherein the plurality of auxiliary particles are formed so as to cover a portion of each of crystal

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faces centered on an edge portion where at least three crystal faces among the polyhedral crystal faces meet.

3. The method of claim 1, wherein the preparing of the mother particle comprises:

mixing a precursor material with deionized water to prepare the first precursor material aqueous solution;

preparing a diluted alkaline solution and loading and stirring the prepared alkaline solution in a reaction container;

mixing the first precursor material aqueous solution in the reaction container and thermal treating the resultant mixture solution; and

cooling the thermally treated mixture solution.

4. The method of claim 3, further comprising mixing an acidic solution to the first precursor material aqueous solution.

5. The method of claim 3, wherein the thermally treating is conducted at a temperature higher than 60° C. and not higher than 100° C. for approximately 2 hours to approximately 24 hours.

6. The method of claim 5, wherein the thermally treating temperature rises at a rate of approximately 0.2° C./min to approximately 1° C./min.

7. The method of claim 1, wherein the forming of the auxiliary particles comprises:

adding and stirring an alkaline solution in a mixture solution in which the mother particle is mixed;

mixing the second precursor material aqueous solution prepared by mixing a precursor material with deionized water in the mixture solution in which the mother particle is mixed;

thermally treating the mixture solution; and

cooling the thermally treated mixture solution.

8. The method of claim 7, wherein the thermally treating is conducted at a temperature higher than 60° C. and not higher than 100° C. for approximately 2 hours to approximately 24 hours.

9. The method of claim 8, wherein the thermally treating temperature rises at a rate of approximately 0.2° C./min to approximately 1° C./min.

10. The method of claim 2, further comprising repeating the adjusting of the size of the auxiliary particles at least one time.

11. The method of claim 10, wherein the adjusting of the size of the auxiliary particles comprises:

adding and stirring an alkaline solution in a mixture solution in which an abrasive particle including the mother particle and the auxiliary particles formed on the surface of the mother particle is mixed;

mixing a third precursor material aqueous solution prepared by mixing a precursor material with deionized water in the mixture solution in which the abrasive particle is mixed;

thermally treating the mixture solution; and

cooling the thermally treated mixture solution.

12. The method of claim 11, wherein the thermally treating is conducted at a temperature higher than 60° C. and not higher than 100° C. for approximately 2 hours to approximately 24 hours.

13. The method of claim 12, wherein the thermally treating temperature rises at a rate of approximately 0.2° C./min to approximately 1° C./min.

14. The method of any of claim 1, wherein the auxiliary particles adjacent to each other are spaced apart from each other or contact each other.

15. The method of claim 14, wherein the plurality of auxiliary particles contacting each other have an overlapping

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height ranging from approximately 0% to approximately 70% to a maximum height thereof.

16. The method of claim **14**, wherein each of the mother particle and the auxiliary particles comprises a ceria particle.

17. The method of claim **1**, wherein the auxiliary particle to the mother particle is formed at a size ratio of approximately 100:1 to approximately 5:1. 5

18. The method of claim **17**, wherein the abrasive particle is formed to have an average particle diameter ranging from approximately 6 nm to approximately 350 nm. 10

19. The method of claim **18**, wherein the mother particle has an average particle diameter of approximately 5 nm to approximately 300 nm and the auxiliary particle has an average particle diameter of approximately 1 nm to approximately 50 nm. 15

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